



THE PREPARATION, PROPERTIES,  
CHEMICAL BEHAVIOR, AND IDENTIFICATION OF  
ORGANIC CHLORINE COMPOUNDS



By ERNEST HAMLIN HUNTRESS

A Brief Introduction to the Use of Beilstein's  
Handbuch der organischen Chemie

The Preparation, Properties, Chemical Behavior, and  
Identification of Organic Chlorine Compounds  
Tables of Data on Selected Compounds of Order III

By ERNEST HAMLIN HUNTRESS and the late SAMUEL PARSONS MULLIKEN  
Identification of Pure Organic Compounds  
Tables of Data on Selected Compounds of Order I  
(Compounds of Carbon with Hydrogen or with Hydrogen and Oxygen)

THE PREPARATION, PROPERTIES,  
CHEMICAL BEHAVIOR, AND IDENTIFICATION OF  
**ORGANIC CHLORINE  
COMPOUNDS**

*Tables of Data on  
Selected Compounds of Order III*

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## PREFACE

This volume represents the second to appear in the series of Tables of Data prepared by the present author. It presents in organized and conveniently usable form a summary of data on a selected list of organic compounds containing carbon and chlorine, or carbon, oxygen, and chlorine, or carbon, hydrogen, and chlorine, or carbon, hydrogen, oxygen, and chlorine. Such compounds may more briefly be described as comprising Order 3.

Although users of its predecessor will immediately recognize many aspects of similarity in this book, they will also note in this volume certain differences. These distinctions are more fully discussed in Chapter I, but certain general aspects may be noted here.

Whereas the treatment of Order 1 compounds was directed mainly toward the aspect of identification, and though this point of view is vigorously continued, the present treatment of compounds of Order 3 has been expanded to include also the preparation, properties, and general chemical behavior of the individuals selected for treatment.

A second major difference from the earlier volume is in the extent of reference to the original literature or the corresponding abstracts thereof. This documentation is carried to a degree which may suggest to organic chemists that this volume comprises a Beilstein. The author hastens to disclaim any such degree of completeness for this work but does admit that for each compound selected a meticulous search of the literature through 1945 has furnished the basis for appropriate selection and systematic grouping of the aspects to be treated.

A third important difference from the earlier volume is the inclusion of references to patents as well as scientific articles. Though such patent references are treated with reserve, it is believed that they will be of interest to all users and of special value to industrial chemists. Throughout the book emphasis is given to industrial aspects since the rapid growth of this field during the last two decades, particularly in the United States, has resulted in the production and large-scale utilization of many individual compounds of this order (3).

A fourth type of difference in the present treatment as compared with that of Order 1 is seen in the tabulation of physical constants. In the earlier volume an attempt was made to select the "best" values. This process tended to conceal the magnitude and nature of the available constants from



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## DATA ON INDIVIDUAL COMPOUNDS

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# ABBREVIATIONS

$[\alpha]_D^{20}$	A specific rotation at 20° for D line	aq. arom. assoc.(d) (n)	water or aqueous aromatic associate(s) (associated) (association)
$\bar{A}$	represents acid residue in whose description it occurs	B	represents a molecule of the "basic" salt- forming compound in whose description it occurs
abs.	absolute; absolutely	B.B.No.	bromide-bromate num- ber
abt.	about	bibl.	bibliography
abund.	abundant	bkn.	"broken" (cf. color ter- minology)
abv.	above	boilg.	boiling
Ac	acetyl radical, i.e., $\text{CH}_3\text{CO}-$	b.p.	boiling point (at atm. pressure unless speci- fied)
AcOEt	ethyl acetate	Bu	n-butyl
AcOH	acetic acid (glacial ace- tic acid when unmodi- fied)	bril.	brilliant
Ac <sub>2</sub> O	acetic anhydride	brn.	brown
ao.	acid	Bz	benzoyl, i.e., $\text{C}_6\text{H}_5\text{CO}-$
aco.	according	BzOH	benzoic acid
acid.	acidify, acidified, acidi- fication	C	Centigrade degrees
act.	active	$\bar{C}$	used to designate the compound in whose description it occurs
addn.(l)	addition (additional)	calc.(d) (n)	calculate(d) (calculation)
adj.	adjacent (e.g., 1,2,3)	cap.	capillary
alc.	alcohol (95% unless otherwise stated); al- coholic	cat.	catalyst; catalytic; catalyzed
ald.	aldehyde	cc.	cubic centimeter(s)
alk.(y)	alkali; alkaline; (alka- linity)	cf.	compare
alm.	almost	cg.	centigram(s)
Am	amyl	charac.	characteristic
ammon.	ammoniacal	chem.	chemical
amorph.	amorphous	cis-	stereochemical opposite of trans-
amt.(s)	amount(s)	cm.	centimeter(s)
anal.	analysis; analyses		
anhyd.	anhydrous		
anti-	anti (stereomeric oppo- site of <i>syn</i> -)		
apprec.	appreciable; appreci- ably		
approx.	approximate; approxi- mately		



coeff.	coefficient	diam.	diameter
col.(n)	color (coloration)	diff.	different; difference; difficultly
comb.(d)(n) (g)	combine(d) (combination) (combining)	dil.(td) (tg) (n)	dilute (diluted) (diluting) (dilution)
comml.	commercial	dimin.	diminish; diminishing; diminished; diminutive
compd.	compound	dis.(lvd)	dissolve (dissolved)
compn.	composition	dissoc.(d) (g) (n)	dissociate(d) (dissociating) (dissociation)
conc.(d) (n)	concentrate(d) (concentration)	dist.(d) (g) (n)	distil(l)ed (distilling) (distillation)
condens.	condensation	distrib.(n)	distribute (distribution)
cond.	condition(s)	div.(n)	divide (division)
confm.(n)	confirm; confirmatory (confirmation)	dk.	dark
const.	constant	d,l-	racemic (by external compensation as contrasted with <i>meso</i> )
cont.(s) (g)	contain(s) (containing)	D.V.	Duclaux Value
conv.(n)	convert (conversion)		E
cor.	corrected		easily
corresp.	corresponding		effervesce(s); effervescent
C.P.	chemically pure		equivalent
cpd.	compound		especially
crit.	critical		estimate(s) (estimated) (estimating) (estimation)
cryst.(n) (d)	crystal(s); crystallize(s) (d); crystalline (crystallization)		Et
C.S.T.	critical solubility temperature		ethyl, i.e., $\text{CH}_3\text{CH}_2$ —
	D		ethyl alcohol (generally refers to 95% if unmodified)
①	derivative (used to introduce important derivatives for specific characterizations)		ether (generally means ordinary diethylether)
(D)	dark (following name of a broken color)	Et	
$D_4^{20}$	density at 20° referred to water at 4°	EtOH	
d-	dextrorotatory	eth.	
dec.(d) (n)	decompose(s) (decomposed) (decomposition)	evap.(d) (g) (n)	evaporate(d) (evaporating) (evaporation)
deliq.	deliquesce(s), deliquescent	evol.(n)	evolve(s) (evolution)
depolym.(d) (n)	depolymerize(s) (depolymerized) (depolymerization)	exam.(d) (n)	examine(d) (examination)
deriv.(s) (d) (n)	derivative(s) (derived) (derivation)	expt.(l)	experiment(al)
desic.	desiccator; desiccated	ext.(d) (g) (n)	extract(s) (extracted) (extracting) (extraction)
detectn.	detection		F
detn.(d)	determine; determination (determined)	fil.(n)	filter(s); filtrate (filtration)
		floc.	flocculate; flocculent
		fluores.	fluoresce(s); fluorescent

f.p.	freezing point	insol.(y)	insoluble (insolubility)
freq.	frequently	irreg.	irregular
fract.(n) (nl)	fraction; fractionate (fractionation) (fractional)	irrit.(n)	irritating (irritation)
		isom.(d) (n)	isomer; isomerize (isomerized) (isomerization)
fum.	fumaroid (stereochemical opposite of maleinoid)		
fumg.	fuming		K
fus.(n)	fuse(s), melt(s); fusible; fusing (fusion)	k	ionization constant
	G	(L)	L
g.	gram(s)		Light (modifying name of a broken color)
gem.	geminate (said of two like groups attached to same atom)	l-	laevorotatory
		l.	liter(s)
geom.	geometrical	lft(s).	leaflet(s)
glac.	glacial	lgr.	ligroin
gr.	green	liq.	liquid; liquefy
grad.	graduate; graduated; gradually	lt.	light (of a color)
gran.	granular; granulated		
		(M)	M
			medium (modifying name of a broken color)
	H	m.	melt(s)
H.E.	hydrolysis equivalent	m-	meta
hexag.	hexagon, hexagonal	mal.	maleinoid (stereochemical opposite of fumaroid)
hr.(s)	hour(s)		
ht.(d) (g)	heat(ed) (heating)	max.	maximum
hydrol.(g) (zd)	hydrolyze; hydrolysis; (hydrolyzing) (hydrolyzed)	Me	methyl, i.e., CH <sub>3</sub> —
		MeOH	methanol, i.e., CH <sub>3</sub> OH
bygros.	bygrosopic	m.e.	milliequivalent
		mg.	milligram(s)
	I	mic.	micro
ibid.	in the same place	microcryst.	microcrystalline
ident.	identical; identity	min.	minute(s); minimum
identif.(d) (n)	identify (identified) (identification)	minl.	mineral
		misc.	miscellaneous; miscible
i.e.	that is	mixt.	mixture(s)
immed.	immediate; immediately	mod.	moderate
impt.	important	modifn.	modification
inact.	inactive; inactivated	mol.	molecular
indef.	indefinite	monoclin.	monoclinic
indic.	indicate; indicator; indicated	ml.	milliliter
		mm.	millimeter
inf.	infinite	m p.	melting point
inorg.	inorganic	ms	meso-

<b>N</b>			
<i>N</i>	normal (equivalents per liter)	pr.	prism(s)
"	normal	pract.	practically
$n_D^{20}$	refractive index at 20° for D line of sodium	prep.(d) (g) (n)	prepare(d) (preparing) (preparation)
ndl.(s)	needle(s)	pres.	presence
neg.	negative	press.	pressure
Neut. Eq.	neutralization equivalent	prim.	primary
neut.(zd)	neutral (neutralized)	prin.	principal
no.	number	prismat.	prismatic
non-fus.	non-fusible	prob.	probably
non-vol.	non-volatile	proc.	procedure
		prod.	product; produce; produced
		prop.	property; properties
		pt.(s)	part(s)
		pulv.(d)	pulverize(d)
		pung.	pungent
		purif.(d) (g) (n)	purify (purified) (purifying) (purification)
<b>O</b>			
o-	ortho		
obs.(d) (n)	observe(d) (observation)		
obt.(d)	obtain(ed)		
opt.	optical		
optim.	optimum	quad.	quadratic
or.	orange	qual.	qualitative; qualitatively
ord.	ordinary		
orig.	original; originally	quant.	quantity; quantitative; quantitatively
org.	organic		
oxid.(g) (n)	oxidize(s) (oxidizing) (oxidation)	quat.	quaternary
		q.v.	quod vide (which see)
<b>P</b>			
Ⓟ	preliminary test		
p-	para	rac.	racemic
perm.	permanent	rap.	rapid; rapidly
pet.	petroleum	reactn.	reaction(s)
Ph	phenyl, i.e., $C_6H_5-$	reagt.(s)	reagent(s)
phys.	physical	rearr.	rearrange(s); rearrangement
physiol.	physiological		
Ek	picryl, i.e., 2,4,6-trinitrophenyl-	recommnd.	recommend; recommended
PkOH	picric acid	recryst.(d) (g) (n)	recrystallize(d) (recrystallizing) (recrystallization)
pl.	plate(s)		
polym.(n)	polymer; polymerize; polymerized (polymerization)	rect.	rectangular
		redis.	redissolve
pos.	positive	reduc.(d) (g) (n)	reduce(d) (reducing) (reduction)
powd.	powder; powdered	ref.	reference
ppt.(d) (g) (n)	precipitate(d) (precipitating) (precipitation)	reminis.	reminiscent
		reppt.(d) (g) (tn)	reprecipitate(d) (reprecipitating) (reprecipitation)
Pr	propyl		

resid.	residue; residual		T	Numbered Test
resin.	resinify; resinification		tbl.(s)	tablet(s); tabular
resp.	respectively		tech.	technical
rbomb.	rhombic		temp.	temperature
	S		theor.	theoretical
Sap. Eq.	saponification equivalent		therm.	thermometer
sapoa.(d) (g) (a)	saponify (saponified) (saponifying) (saponi- fication)		T.N.B.	1,3,5-trinitrobenzeao
			T.N.T.	2,4,6-trinitrotolucae
sat.(d) (g) (a)	saturate(d) (saturating) (saturation)		ter-	tertiary
sec.	second(s)		trans-	stereochemical opposite of cis-
sec.	secondary		transf.	transfer; transform
sect.	section		tt.	test tube
sep.(d) (g) (n)	separate(d) (separating) (separation)			U
sft.(n)(s)	soft; soften(s)		u.c.	uncorrected
shak.(g) (a)	shako(shaking) (shaken)		undec.	undecomposed
siat.(d)	siater(s) (sintered)		undislvd.	undissolved
sl.	slightly		unoxid.	unoxidized
sld. cap.	sealed capillary		unsat.	unsaturated
S.N.	system number (Beil- stein)		unsym.	unsymmetrical
			U.S.P.	United States Pharma- copœia
spar.	sparing; sparingly		u.v.	ultra violet
sol.(a) (y)	soluble (solution) (solu- bility)			V
solv.	solvent(s)		vac.	vacuum
sp gr.	specific gravity		vap.	vapor; vaporizo
sq.	square		var.	variable
subl.(g)	sublimes; sublimate; subliming; sublima- tion		vic.	vicinal (adjacent)
subl. w.m.	sublimes without melt- ing		vig.	vigorous; vigorously
subseq.	subsequent		viol.	violent; violently; vio- let
subet.	substance; substanti- ally; substituted		visc.	viscous
suff.	suffices; sufficient		volat.(g) (n)	volatile (volatilizing) (volatilization)
supersat.(d)(g)(n)	supersaturate(d)(super- saturating) (super- saturation)		volumin.	voluminous
st.	steam			W
st.	sealed tube		warm.	warming
stdg.	standing		wh.	white
sym.	symmetrical		wt.	weight
sym-	stereochemical opposite of anti-			Y
yst.	system; systematic; systematically		yel.	yellow



## MEMORANDUM OF CERTAIN 1946-1947 REFERENCES NOT INCORPORATED IN REGULAR TEXT

The regular text of this book is made up of references selected from the chemical literature through the year 1945. Owing to the disturbed postwar conditions of the publishing and printing trades, and also to the exceptional difficulty and magnitude of this work, almost three years have elapsed since the termination of the period of writing of the organized text. Inevitably, there have appeared during this period many scientific papers whose content would gladly have been incorporated appropriately in the regular text. For practical reasons, however, such continuous adjustment was obviously impossible.

In an effort to avoid so far as possible complete loss of such material, however, certain of the more important papers which have come to the attention of the author during the 1946-1947 period have been listed in the following supplementary bibliography. Articles relevant to more than a single numbered compound are cited under the first in such a numerical series, cross-references being given under subsequent compounds to avoid excess duplication of references. In the interests of brevity, clarity, and consistency of nomenclature, slight modifications of the actual titles of the original papers have sometimes been made for purposes of this listing.

### General

- (1) Table of azeotropes and nonazeotropes  
*Hopkins, Ind. Eng. Chem., Anal. Ed.* **19**, 500-500 (1947)  
 . . . . . its accompanying formula index and  
 . . . . . valuable and includes so many of the  
 . . . . . that it is placed at the head of this supplementary reference list without further cross-reference to it from subsequent entries below.
- 3:0075  $\delta$ -Chloro-*n*-valeric acid  
 (2) Isomeric chlorinated long-chain esters  
*Guest, J. Am. Chem. Soc.* **69**, 300-302 (1947)  
 —Methyl  $\delta$ -chloro-*n*-valerate: b.p. 89-92° at 18 mm. [From  $\delta$ -chloro-*n*-valeronitrile 80%  $H_2SO_4$  refluxed 50 hr.]
- 3:0235  $\alpha$ -Chloroisobutyric acid  
 (3) The chloro- and bromoisobutyronitriles  
*Stevens, J. Am. Chem. Soc.* **70**, 166 (1948)  
 Ⓓ  $\alpha$ -Chloroisobutyramide: cryst. from EtOAc, m.p. 115-118°; from aq., m.p. 117-119°.  
 [From  $\alpha$ -chloroisobutyryl chloride (3:5385) with conc.  $NH_4OH$  at 10° in 70% yield]
- 3:0280 Chloromaleic anhydride  
 (4) Use of  $\bar{C}$  in determination of conjugated diolefins  
*Putnam, Moss, Hall, Ind. Eng. Chem., Anal. Ed.* **18**, 628-630 (1946)

- [illegible]

- (29) Determination of C as spray residue on fresh fruit by three independent methods  
Wichmann, Patterson, Clifford, Klein, Claborn, *J. Assoc. Offic. Agr. Chemists* 29,  
188-190 (1946); *C.A.* 40, 6705 (1946)
- Method 1. Organic chlorine determinations  
Klein, Wichmann, *ibid.* 29, 191-195 (1946); *C.A.* 40, 6705 (1946)
- Method 2. The Shechter-Haller colorimetric procedure  
Clifford, *ibid.* 29, 195-206 (1946); *C.A.* 40, 6705 (1946)
- Method 3. 2,4-Dinitrophenylhydrazine method  
Claborn, Patterson, *ibid.* 29, 206-218 (1946); *C.A.* 40, 6705 (1946)
- (30) Decomposition and volatility of C̄ and some of its derivatives  
Wichmann, Patterson, Clifford, Klein, Claborn, *J. Assoc. Offic. Agr. Chemists* 29,  
216-222 (1946); *C.A.* 40, 6710 (1946)
- (31)  
  
-53 (1947)
- (32)
- (33) Determination of C̄ by Shechter procedure, particularly in milk and fats  
Clifford, *J. Assoc. Offic. Agr. Chemists* 30, 337-349 (1947); *C.A.* 41, 6839 (1947)
- (34) Nature of the hy-products in technical C̄  
Gäzi, Stammbach, *Helv. Chim. Acta*, 29, 563-572 (1946), *Experientia* 1, 276 (1945).  
*C.A.* 40, 5040-5041 (1946)
- (35) Simple purification procedure for C̄  
K. H. Cook, W. A. Cook, *J. Am. Chem. Soc.* 68, 1663-1664 (1946)
- (36) Applications of infrared spectroscopy to C̄  
Downing, Freed, Walker, Patterson, *Ind. Eng. Chem., Anal. Ed.* 18, 461-467 (1946)
- (37) Some derivatives of C̄  
Backeberg, Marus, *J. Chem. Soc.* 1945, 803-805; *C.A.* 40, 1156, 5717 (1946)
- (38) Bromine analogs of C̄  
Cristol, Haller, *J. Am. Chem. Soc.* 68, 140-141 (1946)
- (39) Crystal structure of C̄ and relatives  
Wild, Brandenberger, *Helv. Chim. Acta* 29, 1024-1040 (1946), *C.A.* 41, 42S (1947)
- (40) Syntheses of some analogs of C̄  
Kirkwood, Dacey, *Can. J. Research* 24-B, 69-72 (1946); *C.A.* 40, 5717 (1946)
- (41) Catalytic decomposition of C̄  
Fleener, *J. Am. Chem. Soc.* 68, 2393 (1946)
- (42) Inhibition of catalyzed thermal decomposition of C̄  
Gunther, Tow, *J. Soc. Chem. Ind.* 66, 57-59 (1947), *C.A.* 41, 5675 (1947)
- (43) Dehydrohalogenation of C̄  
Wain, Martin, *Nature* 159, 68-69 (1947); *C.A.* 41, 2715 (1947)
- (44) Estimation of C̄ by methods depending upon dehydrohalogenation  
Wain, Martin, *Analyst* 72, 1-6 (1947); *C.A.* 41, 2198 (1947)
- (45) Preparation of di-(p-chlorophenyl)acetic acid from C̄  
Grummitt, Burk, Egan, *Org. Synthesis* 26, 21-23 (1946)
- (46) Reactions of C̄ and associated compounds  
Forrest, Stephenson, Waters, *J. Chem. Soc.* 1946, 333-339; *C.A.* 40, 5035-5040 (1946)
- (47) Crystallization of C̄ from binary melts  
Gulpin, McCrone, Smedal, Grant, *J. Am. Chem. Soc.* 70, 208-211 (1947)
- 3:3376** 1,1-Dichloro-2,2-di-(p-chlorophenyl)ethane ("DDD")
- (48) Anhydrous FeCl₃ as rearrangement catalyst for some chlorinated diphenylethenes  
Floek, *J. Org. Chem.* 12, 70-712 (1947)
- 3:3380** 4,4-Dichlororesorcinol
- (49) For preparation of isomeric 2,4-dichlororesorcinol see  
Peetevin, Kuchina, *J. Gen. Chem. (U.S.S.R.)* 17, 278-282 (1947); *C.A.* 42, 534-535  
(1948)
- 3:3384** p-Phenylenecarbonyl chloride
- (50) Conversion of C̄ to p-phenylene carbonyl iodide  
Rheinholdt, Perrier, *J. Am. Chem. Soc.* 69, 3145-3149 (1947)
- 3:4053** 2,4-Dichlorophenoxyacetic acid
- (51) Preparation of C̄ from phenol and chlormaleic acid  
Ebel, Bell, Fies, Kaye, Berkshille, *J. Chem. Education* 24, 442 (1947)



- (52) . . . . .
- (53) . . . . .
- (54) Freed, *J. Am. Chem. Soc.* **98**, 2112 (1949)
- 3:4375 *p*-Chlorophenoxyacetic acid  
(—) See reference (53) under 3:4095 (above).
- 3:4410 *cis*-1,2,3,4,5,6-Hexachlorocyclohexane  
(55) Preparation of the benzene hexachlorides  
Gunther, *Chemistry & Industry* **1946**, 399; *C.A.* **41**, 1625 (1947)
- (56) . . . . .
- (57) . . . . .
- (58) Alkaline degradation of benzene hexachlorides  
Gunther, Blinn, *J. Am. Chem. Soc.* **69**, 1215-1216 (1917)
- (59) The gamma isomer of hexachlorocyclohexane  
Slade, *Chemistry & Industry* **1945**, 314-319; *C.A.* **40**, 2257-2259 (1946)
- (60) The epsilon isomer of hexachlorocyclohexane  
Kauer, DuVall, Alquist, *Ind. Eng. Chem.* **39**, 1334-1338 (1947)
- (61) Determination of hexachlorocyclohexane in impregnated cloth  
Goldenson, Sass, *Ind. Eng. Chem., Anal. Ed.* **19**, 320-322 (1947)
- 3:4612 Di-(*p*-chlorophenyl)acetic acid  
(—) Preparation from "DDT"; see reference (45) under 3:3298 (above)
- 3:4835 Hexachloroethane  
(92) Preparation of C by chlorination of liquid 1,1,2,2-tetrachloroethane and pentachloroethane  
Pearce, *Can. J. Research* **24-F**, 369-379 (1946); *C.A.* **49**, 7151 (1946)
- 3:4917 Tetrachlorophthalic anhydride  
(63) Reactions and uses of C  
Lawlor, *Ind. Eng. Chem.* **39**, 1419-1423 (1947)
- (64) . . . . .  
17)
- (65) Nordlander, Cass, *J. Am. Chem. Soc.* **69**, 2679-2682 (1947)
- 3:4990 *trans*-1,2,3,4,5,6-Hexachlorocyclohexane  
(—) See references (55)-(91), inclusive, under *cis*-isomer (3:4419) (above)
- 3:5099 Carbonyl chloride (Phosgene)  
(66) Heat capacity, entropy, vapor pressure, and heats of fusion and vaporization of C  
Gisquet, Jones, *J. Am. Chem. Soc.* **70**, 120-124 (1948)
- (67) . . . . .  
38, 624-626 (1946)
- (68) . . . . .  
ons for formation of tetrasubstituted ureas  
Lastovskii, *J. Applied Chem. (U.S.S.R.)* **10**, 440-444 (1940); *C.A.* **41**, 1214 (1947)
- (69) Reaction of C with *o*-aminobenzoic acid (to give 72-75% yield isatoic anhydride)  
Wagner, Fegley, *Org. Syntheses* **27**, 45-47 (1947)
- 3:5028 *trans*-1,2-Dichloroethylene  
(79) . . . . .  
)
- (71) . . . . .
- 3:5942 *cis*-1,2-Dichloroethylene  
(—) See references (70) and (71) under *trans*-isomer (3:5028) (above)
- 3:5050 . . . . .  
(72) . . . . .  
69, 1190-1195 (1947)
- (73) . . . . .  
Chem. Soc. **69**, 3045-3047 (1947)



- 3:5550 **1,3-Dichlorobutene-2**  
 (88) Oxidation of  $\bar{C}$  with aqueous  $HNO_3$  or  $Ca(NO_3)_2$   
 Isagulyants, Mkryan, *Bull. Armenian Branch Acad. Sci. U.S.S.R.*, 1944, No. 5/6,  
 17-21; *C.A.* 40, 3394 (1946)  
 (89) *Sci. U.S.S.R.*, 1944, No. 5/6,  
 75-78; *C.A.* 40, 3394 (1946)  
 (90) Gaseous products of action of zinc dust on  $\bar{C}$   
 Tatevosyan, Vardanyan, *Bull. Armenian Branch Acad. Sci. U.S.S.R.*, 1941, No. 8,  
 75-78; *C.A.* 40, 3394 (1946)  
 (91) Reaction of  $\bar{C}$  with aromatic hydrocarbons  
 Isagulyants, Muscheghian, *Compt. rend. acad. sci. U.R.S.S.* 56, 165-168 (1947);  
*C.A.* 42, 530 (1948)
- 3:5552 **2-Chloroethanol-1 (ethylene chlorohydrin)**  
 (92) Determination of  $\bar{C}$  (by hydrolysis and determination of chloride ion)  
 Uhrig, *Ind. Eng. Chem., Anal. Ed.* 18, 469 (1946)  
 (93) Preparation and properties of  $\beta$ -chloroethyl esters of boric, silicic, and phosphoric acids  
 Jones, Thomas, Pritchard, Bowden, *J. Chem. Soc.* 1946, 824-827; *C.A.* 41, 390-391  
 (1947)  
 (94) Analysis of water-soluble chlorohydrins  
 Trafelet, *Analytical Chemistry* 20, 68-69 (1948)
- 3:5590 **1,3-Dichloro-2-methylpropene-1**  
 (95) Preparation of *cis* and *trans* isomers of  $\bar{C}$   
 Hatch, Russ, Gordon, *J. Am. Chem. Soc.* 69, 2614-2616 (1947)
- 3:5633 **3-Chloro-2-(chloromethyl)propene-1**  
 (—) See reference (95) under 3:5590 (above)
- 3:5725 **1,1,1,2-Tetrachloroethane**  
 (—)  
 (—)
- 3:5750 **1,1,2,2-Tetrachloroethane (acetylene tetrachloride)**  
 (96) *Sci. U.S.S.R.*, 1946, No. 5/6, 17-21; *C.A.* 41, 1578 (1947)  
 (97) Goldenson, Thomas, *J. Ind. Hyg. Toxicol.* 29, 14-22 (1947); *C.A.* 41, 1578 (1947)  
 (—) Chlorination of  $\bar{C}$  as source of hexachloroethane  
 See reference (62) under 3:4835 (above)
- 3:5880 **Pentachloroethane**  
 (—) Chlorination of  $\bar{C}$  as source of hexachloroethane  
 See reference (62) under 3:4835 (above)
- 3:5885 **1,2,3-Trichloro-2-methylpropane**  
 (—) See reference (95) under 3:5590 (above)
- 3:5900 **1,3-Dichlorobutanone-2**  
 (98) Formation of  $\bar{C}$  from ethyl methyl ketone by vapor-phase chlorination  
 Rabjohn, Rogier, *J. Org. Chem.* 11, 781-787 (1946)
- 3:5910  **$\alpha,\alpha,\beta$ -Trichloro-*n*-butyraldehyde ("Butyrchloral")**  
 (99) Reaction of  $\bar{C}$  with Grignard reagents  
 Floutz, *J. Am. Chem. Soc.* 68, 2490-2491 (1946)
- 3:5960 **1,1,2,2-Tetrachloroethane**  
 (100) *Sci. U.S.S.R.*, 1946, No. 5/6, 17-21; *C.A.* 41, 1578 (1947)
- 3:5985 **1,3-Dichloropropanol-2 (" $\alpha$ -dichlorohydrin")**  
 (101) Activated  $\bar{C}$ ; a new colorimetric reagent for vitamin A  
 Sobel, Werbin, *Ind. Eng. Chem., Anal. Ed.* 18, 570-573 (1946)  
 (102) Determination of vitamin A with activated  $\bar{C}$ : a comparison with spectrophotometric  
 and  $SbCl_5$  methods  
 Sobel, Werbin, *Ind. Eng. Chem., Anal. Ed.* 19, 107-112 (1947)

- 3:6207 Ethyl  $\alpha$ -chloroacetate**  
 (103) Behavior of  $\bar{C}$  with arylhydrazines  
 van Alphen, *Rec. trav. chim.* **64**, 305-308 (1945); *C.A.* **41**, 407 (1947)
- 3:6550 *p*-Chlorobenzoyl chloride**  
 (194) Conversion of  $\bar{C}$  with pyridine to *p*-chlorobenzoic acid  
 Allen, Kibler, McLachlin, Wilson, *Org. Syntheses* **26**, 1-3 (1946)
- 3:6878 1-Chloronaphthalene**  
 (105) 1-Halonaphthalenes in the Friedel-Crafts reaction  
 Jacobs, Winstein, Ralls, Robson, *J. Org. Chem.* **11**, 27-33 (1946)
- 3:7005 Methyl chloride**  
 (106) Determination of  $\bar{C}$  in air  
 Franklin, Gunn, Martin, *Ind. Eng. Chem., Anal. Ed.* **18**, 314-316 (1946)  
 (107) Preparation of  $\bar{C}$  (free from dimethyl ether)  
 Pieck, Courtoy, *Bull. soc. chim. Belg.* **56**, 65-71 (1947); *C.A.* **41**, 6524 (1947)
- 3:7010 Vinyl chloride**  
 (108) Condensation of alkyl halides with monohalo-olefins  
 Schmerling, *J. Am. Chem. Soc.* **68**, 1650-1654 (1946)
- 3:7015 Ethyl chloride**  
 (—) See reference (70) under 3:5028 (above)
- 3:7020 2-Chloropropene-1**  
 (—) See reference (108) under 3:7010 (above)
- 3:7025 2-Chloropropane (isopropyl chloride)**  
 (—) See reference (70) under 3:5028 (above)  
 (—) See reference (108) under 3:7010 (above)
- 3:7035 3-Chloropropene-1 (allyl chloride)**  
 (109) . . . . .  
*ans. Am. Inst.*
- (110) Conversion of  $\bar{C}$  with  $\text{AlCl}_3$  to hexadiene-1,5 (diallyl) in 55-65% yield  
 Turk, Chanan, *Org. Syntheses* **27**, 7-9 (1947)
- (111) Condensation of  $\bar{C}$  with aromatic hydrocarbons or aryl halides to give 1-aryl-2-chloro-  
 propanes  
 Patrick, McBee, Hass, *J. Am. Chem. Soc.* **68**, 1000-1011 (1946)  
 (—) See reference (108) under 3:7010 (above)
- 3:7040 1-Chloropropane (*n*-propyl chloride)**  
 (—) See reference (70) under 3:5028 (above)
- 3:7045 2-Chloro-2-methylpropane (*tert*-butyl chloride)**  
 (—) See reference (70) under 3:5028 (above)  
 (—) See reference (108) under 3:7010 (above)
- (112) The  $\text{AlCl}_3$ -catalyzed addition of  $\bar{C}$  to propylene  
 Miller, *J. Am. Chem. Soc.* **69**, 1764-1768 (1947)
- (113) The condensation of  $\bar{C}$  with cyclohexene  
 Schmerling, *J. Am. Chem. Soc.* **69**, 1121-1125 (1947)
- (114) Formation of  $\bar{C}$  by addition of hydrogen chloride to isobutylene  
 Mayo, Katz, *J. Am. Chem. Soc.* **69**, 1339-1348 (1947)
- (115) The hydrolysis of  $\bar{C}$  in 95% water/5% acetone solution  
 Swain, Ross, *J. Am. Chem. Soc.* **68**, 658-661 (1946)
- 3:7065 Acetyl chloride**  
 (116) Ketene dimers from acid halides  
 Sauer, *J. Am. Chem. Soc.* **69**, 2444-2448 (1947)
- 3:7080 2-Chlorobutadiene-1,3 (Chloroprene)**  
 (—) See reference (85) under 3:5350 (above)
- (117) Composition and structure of dimers of  $\bar{C}$   
 Klebanskii, Denisova, *J. Gen. Chem. (U.S.S.R.)* **17**, 703-716 (1947); *C.A.* **42**, 1215  
 (1948)
- 3:7085 Chloromethyl methyl ether**  
 (118) Reaction of  $\bar{C}$  with terpenes  
 Allard, *Bull. soc. chim. France* **1947**, 731-735; *C.A.* **42**, 890 (1948)

- 3:7170 Propionyl chloride  
(—) See reference (100) under 3:5960 (above)  
(—) See reference (116) under 3:7065 (above)
- 3:7210 1-Chlorobutadiene-1,3  
(119) *Synthesis and properties of  $\bar{C}$*   
Petrov, Sopov, *J. Gen. Chem. (U.S.S.R.)* 15, 981-987 (1945); *C.A.* 40, 6406 (1945)  
(—) See reference (85) under 3:5350 (above)
- 3:7220 2-Chloro-2-methylbutane (*ter*-amyl chloride)  
(—) See reference (108) under 3:7010 (above)
- 3:7370 *n*-Butyryl chloride  
(—) See reference (116) under 3:7065 (above)
- 3:7465 4-Chloro-2-methylbutene-2  
(120) Formation of  $\bar{C}$  from isoprene by addition of HCl  
Jones, Chorley, *J. Chem. Soc.* 1946, 832-833; *C.A.* 41, 386 (1947)
- 3:7560 Isovaleryl chloride  
(—) See reference (116) under 3:7065 (above)
- 3:7598 3-Chlorobutanone-2  
(—) See reference (98) under 3:5900 (above)
- 3:7650 1,3-Dichlorobutene-1  
(121) The dichlorobutene prepared from crotonaldehyde  
Andrews, *J. Am. Chem. Soc.* 68, 2584-2587 (1946)
- 3:7865 1,1-Dichlorobutene-2  
(—) See reference (121) under 3:7650 (above)
- 3:7740 *n*-Valeryl chloride  
(—) See reference (116) under 3:7065 (above)
- 3:7747 1-Chloropropanol-2 (propylene chlorohydrin)  
(—) See reference (94) under 3:5552 (above)
- 3:7925 1,3-Dichlorobutane  
(122) Preparation of  $\bar{C}$  and its Friedel-Crafts reaction with benzene  
Sisido, Nozaki, *J. Am. Chem. Soc.* 69, 961-964 (1947)
- 3:8012 1-Chlorobutanone-2  
(—) See reference (98) under 3:5900 (above)
- 3:8110 *d,l*-1-Chlorobuten-3-ol-2  
(123) Some reactions of  $\bar{C}$   
Bissinger, Fredenburg, Kadesch, Kung, Langston, Stevens, Strain, *J. Am. Chem. Soc.* 69, 2955-2961 (1947)
- 3:8168 *n*-Caproyl chloride  
(—) See reference (116) under 3:7065 (above)
- 3:8520 *n*-Heptanoyl chloride  
(124) Conversion of  $\bar{C}$  to *n*-heptanoic anhydride with pyridine  
Allen, Kibler, McLachlin, Wilson, *Org. Syntheses* 26, 1-3 (1946)
- 3:8535  
(125) . . . . . eissgerber, Wilkins, Whitmore, *Ind. Eng.*  
(126) . . . . . in preparation of benzylamines  
(127) . . . . . /l magnesium chloride and diethyl sulfate  
1-2050 (1947)
- 3:8680 *n*-Octanoyl chloride  
(—) See reference (116) under 3:7065 (above)
- 3:9132  $\beta$ -Chloroisobutyric acid  
— $\beta$ -Chloro-isobutyramide: *cryst. from pet. ether/EtOAc, m.p. 102-104°*. [From  $\beta$ -chloroisobutyronitrile by partial hydrolysis with  $H_2SO_4$ ; see reference (3) under 3:0235 (above).]

- 3:9295 5-Chloropentanol-1  
(128)  $n_D^{20} = 1.5169$
- 3:9395 6-Chlorohexanol-1  
(129) Preparation of  $\bar{C}$  and its reactions with amines  
K. N. Campbell, A. H. Sommers, J. F. Kerwin, B. K. Campbell, *J. Am. Chem. Soc.* 68, 1557 (1946)
- 3:9567 Phenylacetyl chloride  
(130) Friedel-Crafts reactions of  $\bar{C}$  with anthracene, phenanthrene, or pyrene  
Hoi, Royer, *Bull. soc. chim.* 1946, 659-661; *C.A.* 41, 3453 (1947)
- 3:9858 *n*-Dodecanoyl chloride (lauroyl chloride)  
(131) Preparation of  $\bar{C}$   
Ackley, Tesoro, *Ind. Eng. Chem.* 18, 444-445 (1946)  
(—) See reference (116) under 3:7065 (above)
- 3:9865 1,1,1-Trichloro-2,2-bis-(*o*-chlorophenyl)ethane ("*o,o'*-DDT")  
(132) Preparation of  $\bar{C}$   
Gätzi, *Helv. Chim. Acta* 29, 1159-1163 (1946); *C.A.* 41, 114-115 (1947)  
(133) Isolation of  $\bar{C}$  from technical DDT  
Cristol, Soloway, Haller, *J. Am. Chem. Soc.* 69, 510-515 (1947)
- 3:9885 *n*-Tetradecanoyl chloride (*n*-myristoyl chloride)  
(—) See reference (116) under 3:7065 (above)
- 3:9960 *n*-Octadecanoyl chloride (*n*-stearoyl chloride)  
(—) See reference (116) under 3:7065 (above)

are also present, a compound is said to belong to a higher order: e.g., compounds of carbon with both hydrogen and nitrogen, with oxygen and nitrogen, or with hydrogen, oxygen, and nitrogen comprise Order 2. A systematic arrangement of still higher orders has been developed but need not be fully amplified here.

The substance of the present volume is concerned primarily with compounds of Order 3, i.e., with compounds containing carbon and chlorine; carbon, oxygen, and chlorine; carbon, hydrogen, and chlorine; or carbon, hydrogen, oxygen, and chlorine. To all such compounds deemed of sufficiently general interest to warrant detailed treatment in this book, serial numbers have been assigned as later explained. Although such serial numbers are thus restricted to species of Order 3, a vast number of compounds belonging to other orders inevitably occurs in the course of the individual texts so that this volume has far wider utility than might at first glance be supposed. At the same time not all substances belonging to Order 3 are given numbers since many are not of sufficient value to warrant such extensive treatment.

## 2. The matter of suborders

In the general plan of ordinal classification, it is sometimes (but not always) useful to effect subdivision of orders into two suborders according to whether or not the pure compounds are colored. For both Orders 1 and 2, such subordering has special merit. For the present Order 3 compounds, however, the proportion of colored individuals is almost negligible, and employment of suborders has been avoided.

## 3. The arrangement of compounds of Order 3 into *divisions*

Just as the individual compounds of Order 1 were ultimately further subclassified into various *genera*, each characterized by a common behavior in certain prescribed and carefully defined *generic tests*, so it would of course be perfectly possible to set up an analogous series of genera for any or all of the higher orders. After considerable reflection and experimentation, however, such extension of the method of generic subclassification has seemed an extravagant formality whose added value for the higher orders does not warrant its establishment. Consequently, the individuals comprising the present Order 3 are not arranged by genera, and there are no standardized generic tests to be systematically applied.

Instead of arrangement by genera, therefore, the compounds assigned serial numbers in this book are arranged in three *divisions*. The first of these divisions comprises members of Order 3 which, when pure, are normally solids with at least reasonably definite melting points. The second comprises members of Order 3 which, when pure, are liquids with boiling points attainable and recorded at ordinary pressure. The third division comprises

### 3 THE SEQUENCE OF COMPOUNDS WITHIN THE THREE DIVISIONS

members of Order 3 which, even when pure, are liquids which either cannot be distilled at atmospheric pressure without serious decomposition or for which such data are available only under reduced pressure. Ample cross-references connecting the solid and liquid divisions facilitate recognition of appropriate cases.

#### 4. The sequence of compounds within the three divisions

**DIVISION A.** The individual solids constituting Division A are arranged in the order of increasing magnitude of their respective melting points. For compounds on which there is poor agreement regarding the true melting point, the value determining the position of the compound relative to its neighbors is not necessarily the highest listed. Values printed within square brackets have been regarded by the author on the collateral evidence as possibly doubtful, and such constants have been discounted in assigning positional sequence to the compound.

**DIVISION B.** This division, comprising liquids of Order 3 with boiling points at ordinary pressure, is (unlike either its predecessor or successor) further subdivided into two sections according to the specific gravity at 20°C. referred to water at 4°C. Section 1 contains such liquids with values of  $D_4^{20}$  greater than 1.15; Section 2 contains correspondingly those liquids for which the value of  $D_4^{20}$  is less than 1.15. Within each of the sections of Division B the individual species are arranged in the order of increasing magnitude of their respective boiling points, preferably at 760 mm. pressure. For compounds whose boiling points at this standard pressure are unreported, no attempt has been made to calculate over since to do so seems likely to introduce serious uncertainties.

**DIVISION C.** This division contains all serially numbered compounds of Order 3 which have not been allocated to either of the preceding divisions, such cases usually comprising liquids for which boiling points are reported only at reduced pressures. Within this division an entirely different method of establishing the listing sequence is employed; viz., the compounds are listed in ascending sequence according to the composition of their empirical formulas. For any given number of carbon atoms, compounds containing carbon and chlorine, or carbon, oxygen, and chlorine, or carbon, hydrogen, and chlorine, or carbon, hydrogen, oxygen, and chlorine fall in that sequence. Within any one of these four subgroups the sequence is determined by increasing magnitude of the number of component atoms in the sequence (as above) of carbon, hydrogen, oxygen, and chlorine. Although expressed in words this sounds formidable, even casual inspection of the Tables or of the Empirical Formula Index quickly supplies convincing evidence of its complete simplicity in actual practice.



## 5. The arrangement of data on individual compounds

Whether the amount of data for the compounds comprising this volume is large or small, and irrespective of numerous variations of details, a certain standard form may be recognized as common to all. This form may be construed as made up of the following five elements:

- A. The heading.
- B. Fundamental physical constants.
- C. General data on other constants, preparation and properties.
- D. Designation of special or preliminary tests.
- E. Derivatives.
- F. References to the original literature.

The relative amount of space devoted to these five aspects varies according to circumstances. Each is discussed below in much further detail.

### A. The heading

The heading of each numbered compound comprises (in its most general form) five components which always occur in the following sequence from left to right, viz.,

1. Location number of compound in this book (Order 3)	2. Name (or names)	3. Structural formula	4. Empirical formula	5. Beilstein reference
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(1) *The location number.* Each compound on which detailed treatment is given in this book has been assigned an arbitrary number to facilitate frequent cross reference in indexes and other parts of the text. This number consists of a digit representing the order of the compound (thus all species of this volume have location numbers beginning with 3), followed by a colon and then a four-digit arbitrary number. The system is, therefore, entirely comparable to a telephone number, the initial digit preceding the colon corresponding to an exchange, the four following digits corresponding to an individual line.

In assigning serial location numbers to the various individuals treated in this book, a principle has been maintained whose recognition greatly facilitates recognition of the physical nature of the corresponding substances. All members of Division 1 (solids) carry numbers between 1 and 4999; all members of Division 2, Section 1, are between 5000 and 6999; all members of Division 2, Section 2, are between 7000 and 8999; all members of Division 3 are between 9000 and 9999.

For a given compound, the full descriptive data are recorded only in one place, i.e., in that corresponding to the location number. When occasion

arises to be reminded in some other portion of the book of certain properties of a given compound, the *heading only* is repeated followed by a cross reference to the place of detailed description, the section usually occupied by the location number being indicated merely by a dash. The most frequent occasion for this type of cross reference is to indicate the boiling point of a compound normally met with as a solid, or alternatively the melting point of a substance normally met as a liquid.

(2) *The name (or names) of the compound.* The second element of the heading is devoted to the name (or names) of the compound. Out of all possible names, one (regarded for the purposes of this book as the "principal name") has been printed in bold-face capitals.

In many instances, however, this principal name is followed in ordinary type by one or more other names which are in common use and which might occur alternatively to users of this volume. All these names are appropriately entered in the alphabetical name index so that the location number is readily obtained irrespective of which name may be sought by the user.

(3) *The structural formula of the compound.* Since it is frequently easier to interpret the chemical reactions of a compound by contemplation of its structural formula rather than its name, such structural pictures are given for all compounds in this volume.

If a particular compound reacts as if it had two different structures, both are pictured.

Although such structural formulations are construed as the third element of the heading of each compound, it may happen that, owing to practical space considerations, the picture is not actually printed as part of the top line but depressed somewhat below it.

(4) *The empirical formula.* The fourth element of the heading is the empirical formula. This will be found useful in many ways, particularly in suggesting (especially with the amplification afforded by the empirical formula index) isomeric compounds from which distinction must be made, and in searching the abstract periodicals for data reported after the publication of this volume.

(5) *The Beilstein reference.* Each compound listed in these *Tables* carries in the upper right-hand corner as the fifth element of the heading reference to Beilstein's *Handbuch der organischen Chemie*. All such references designate the fourth edition of this important tool.

At the time of preparation of these *Tables*, all twenty-seven volumes of the primary series (covering the literature up to 1910) together with the corresponding twenty-seven volumes of the first supplementary series (1910-1919, inclusive) of Beilstein's *Handbuch* were available. For every numbered compound of these *Tables* which appears in either the main or first supple-

mentary series, the Beilstein reference will comprise two parts, the first giving the volume and page in the main series, the second giving corresponding reference to the first supplementary series. To distinguish the latter, the volume reference carries the subscript 1, and the page reference is placed between parentheses to indicate that the regular pagination of such supplementary volume is designated.

In addition to the main and first supplementary series of Beilstein mentioned above, there were also available during the preparation of these *Tables* the first five volumes of the second supplementary series (1920-1929) of Beilstein's *Handbuch*. For such of the present numbered compounds as were treated in this available fragment, the Beilstein reference will, therefore, contain a third element representing the volume and page involved. For this kind of case the volume reference bears the subscript 2 (to indicate second supplementary series) together with the page reference in parentheses as before.

In accordance with the above explanation, a given compound will have either two or three Beilstein references. It is, of course, possible for a compound to have citation to only one or two out of the three maximum possibilities; absence of any data for a particular Beilstein unit is indicated by short dashes after the volume number.

The remaining possible case is that in which the compound in question is of such recent origin that Beilstein contains no reference to it either in the main section or either supplementary series. Many such compounds occur in this Order 3. Under these circumstances the usual Beilstein citation is replaced by the Beilstein System Number of the compound, e.g., Beil. S.N. 644. Such type of reference immediately indicates that no reference to the substance is contained in any Beilstein issues through Vol. V of the second supplementary series. Whenever third, fourth, or later supplementary series become available, however, this system number will indicate the position of the compound within narrow limits, even though volume and page cannot now be predicted.

The practice of giving all three Beilstein citations wherever possible serves as a continual reminder that to look merely in the main series volume of Beilstein yields material only up to 1910; for the next two decades the corresponding first and second supplements must also be examined. In this respect these *Tables of Order 3* extend the practice of those of Order 1, where only the main series citation was made, extension to the first supplement being left to the user.

That these references to Beilstein's *Handbuch* are here included only as an additional convenience to users of these *Tables* should be clearly understood. This book is wholly independent of Beilstein, and those users to whom Beilstein may be inaccessible are reassured that the value of these *Tables* to them is in no way impaired.

*B. Fundamental physical constants*

The five components of the standard heading having been discussed, some comment upon the next element of each description is required. This next element comprises what are here designated as "fundamental physical constants" and which in the most general cases consist of data on (1) the melting point, (2) boiling point, (3) density, and (4) refractive index. In the sequence named, these are arranged in four vertical columns from left to right of a given page. For substances which are solids under ordinary conditions, the melting-point column is the first at the left of the page with the boiling-point column next following in the left central section. For such solids only rarely will density or refractive index data appear. For liquids, however, the first left-hand column is devoted to boiling-point data, the melting points being displaced to the next right-hand column because of their subordinate value in such instances.

(1) *The melting point.* Whereas in the earlier *Tables of Order 1* the general practice was to express only a single figure for this constant, the individual descriptions of this book include substantially all values that have been reported. However, values which in the light of collective subsequent results are certainly too low, or those which because of their wide range make no claim to accuracy, are omitted. The survey of values thus set forth, together with the fact that the source of each value is also given, permits the user to form his own opinion concerning the magnitude, degree of concordance, and precision of the available data.

For each individual compound the several values are arranged in the order of diminishing numerical magnitude. In general the value of highest magnitude is employed to determine the place of the individual solid relative to its fellows (i.e., to determine its serial location number). However, values enclosed by square brackets are regarded by the author on collateral evidence as being abnormally high, and such constants are ignored in establishing the serial number of the individual.

The several melting points are recorded here just as they are reported in the original literature; whenever the designations *corrected* or *uncorrected* were included in the original source, they are repeated here; most of the values, however, fail to specify whether they are corrected or not. This careless usage of much journal literature is to be deplored.

No attempt has been made in this book generally to maintain a distinction between melting point and freezing point. Undoubtedly, most of the values reported represent conventional capillary-tube melting points; frequently, however, the values are expressed to a degree of precision suggesting that a cooling-curve method was employed. Whenever the distinction is of importance, the user can readily ascertain full details from the cited references.

(2) *The boiling point.* In complete analogy with its treatment of melting points, the individual descriptions of this book include substantially all recorded values of the boiling point. These are tabulated in the order of diminishing numerical magnitude of the prevailing pressures. Wherever the data can be found, the value at 760 mm. pressure is cited; however, if this is not directly reported, no attempt has been made to convert the available figures over to that pressure, as to do so would introduce unwarranted assumptions. Values of the boiling point at various pressures are meticulously included in the *Tables*. However, when a careful physicochemical study has been made of the vapor pressure of an individual, selected values are printed and reference made to the original for further detail.

Even a casual examination of the boiling point data reported in this book leads at once to the conviction that there has been a great variation in the precision of measurement of the prevailing pressure over the boiling liquid. In fact an incredible proportion of workers has not reported any pressure figures at all or complacently referred to the "prevailing atmospheric pressure." Even when pressure measurements are reported, the evident general lack of concordance becomes distressing evidence of the inadequacy and inaccuracy of many of the data in the literature.

(3) *Densities.* Unlike the extensive treatment accorded for melting points and boiling points, this book does not attempt to tabulate all possible published values for the densities of liquid compounds. However, all available data for density at 20°C. referred to water at 4°C. are given; and, whenever possible, the same procedure is extended to values for  $D_4^{25}$  and  $D_4^{15}$ . Note that, when values are given for various temperatures, those for the highest temperature are printed at the top of the density column, followed in diminishing magnitude of temperature by the other values. This simple and obvious device is intended to assist users of these *Tables*, but they should be reminded that this plan was not (unfortunately) employed with the *Tables of Order 1*.

Density data are given for all liquids for which they can be found; for compounds normally solid, the density is occasionally given for some temperature above the melting point, especially if refractive index values at the same temperature are also available.

Whenever in an original paper there exists any uncertainty as to the temperature of the water with which comparison is made, the lower subscript is replaced by a short dash to indicate that the omission of this figure is not accidental but is because of inadequate expression in the original. In many or even most such cases it is possible that the author intended to convey that the density was expressed with respect to water at the same temperature. This author, however, declines to make any such assumption and ventures to express the view that research workers and journal editors should insist upon unambiguous expression of such data.

(4) *Refractive indices.* These are usually given in the form  $n_D^{20}$ , i.e., the refractive index determined at 20°C. with the D line of sodium light. In some instances data for other lines of the spectrum have been reported here when no data on the D line were available. As with the densities above, refractive index data are frequently printed for other temperatures, and the same typographical convention of placing the higher-temperature values above the lower-temperature ones is continued.

### *C. General data on other constants, preparation, and properties*

The preceding details of the five components of the heading and the four so-called fundamental constants having been discussed, it is now desirable to comment upon the third element of the text of each compound. The material comprising this third section actually comprises most of the space of this book. Although sometimes consisting of only a few paragraphs, there are many members of Order 3 for which the general exposition of behavior requires many pages. Such extended treatments are frequently (although not invariably) subdivided by major and minor headings intended to facilitate quick recognition of the probable location of particular types of desired information. Careful examination of the text of any typical individual compound will quickly disclose that it has in general been dealt with in generous fashion. At the same time it is obvious that a line must be drawn somewhere. For example, in connection with the discussion of an alkyl halide such as *n*-butyl chloride, it is certainly of highest relevance to indicate the mode and extent of its ability to form *n*-butyl magnesium chloride. Furthermore, the value of the simpler reactions of the RMgCl compounds, particularly with reference to their utility in the identification of the initial halide itself, is evident, but on the other hand no attempt has been made to cover all the known reactions of butyl magnesium chloride since that would involve an undertaking of disproportionate magnitude.

Although details of the texts of individual compounds naturally differ in nature and magnitude and are influenced by the literature content corresponding to the direction of published research, certain aspects occur with sufficient frequency to warrant comment.

The text of each compound invariably comprises its methods of preparation and its chemical behavior. For many of the more common or especially important species, these two aspects are often preceded by an introductory section containing certain physical data (in addition to that of the heading) likely to be of particular interest or utility to organic chemists. Examples of such entries include binary and ternary systems with other compounds, especially with reference to freezing-point composition data, azeotropes, densities and/or refractive indices, etc. In this introductory section also attention is frequently directed to methods of quantitative determination

of the compound, examples of industrial or other utilization, biochemical behavior especially with regard to studies on toxicity, antiseptic character, etc. The selection of entries for this introductory section is admittedly arbitrary, and users are reminded that this book makes no claim to include all known data even on the compounds to which serial numbers are assigned. Indeed, in an effort to keep the volume within reasonable bounds, certain types of data of value to organic chemists have been deliberately (though regretfully) excluded, such as references to absorption or Raman spectra, dipole moments, and viscosities, although many instances of the four fundamental physical constants of the heading are drawn from original publications primarily concerned with these aspects.

Within the text of each individual numbered compound (immediately following the above-mentioned introductory section, if any), there occurs a section on its methods of preparation. This treatment has purposely been made as complete as possible. To a limited degree distinction has been made between preparation and formation; but, because even in contemporary publications many authors fail to report yields, adequate recognition of the appropriate category is not always possible. Original results reported only in terms of weight have been calculated over to percentage yields. Variations in yields by a single method of preparation are contrasted by massing them in the text, the uniform practice of following each statement with its corresponding citation serving conveniently to associate each yield with a particular modification. With compounds for which there are many modes of preparation, the most generally practicable methods are often singled out for particular mention at the beginning of the preparative section, followed by a systematic presentation of all the recorded methods under various sub-headings appropriate to the circumstances.

Users of this book will find these sections on preparation not only extremely useful from the viewpoint of comparison of various alternatives but also very stimulating and suggestive in the formulation of unconventional approaches to their particular problems.

Within the text of each numbered compound of this book, following the introductory section (if any) and the preparative section, is next set forth the significant aspects of its chemical behavior. The length of this part of the treatment varies widely from a few phrases to many pages. Very long treatments are appropriately subdivided for practical convenience, the particular sequence of arrangement being dictated by various circumstances. For example, the earlier subdivisions often deal with pyrolysis, reduction, oxidation, and substitution reactions, followed by the behavior with inorganic and organic reactants. With bifunctional compounds the initial group is frequently followed by the behavior of each function with inorganic and organic reactants in that order. Users will experience no difficulty in recognizing

the systematic organization of each compound. Emphasis has been placed upon a systematic and logical presentation of each case, and the above general outline has served the construction of this book only as a general guide rather than a rigid frame.

Two matters continually arising within the descriptive text deserve a further word of comment. The first relates to the fact that, in the course of reporting the chemical behavior of each numbered compound, there is necessarily involved reference to many other substances. Such of these as appear in either this volume (Order 3) or its predecessor (Order 1) are immediately followed by their serial numbers. A great many other compounds belonging to orders not yet written up in this series are inevitably involved; for such compounds reference to Beilstein is usually made for the convenience of the user who may have occasion to follow the matter further.

The second matter involves the practice of this book with respect to citations. Many instances appear which at first glance might appear to involve unnecessary repetition of the citation number, but which really comprise signals to the reader. As a simple illustration, consider the following extract from the text of *p*-chlorophenol, referring to the method of preparation of its *N*-(*m*-nitrophenyl)carbamate, viz.: "From  $\bar{C}$  with *m*-nitrobenzazido (283) or *m*-nitrophenyl isocyanate (283) in lgr. (283)." This usage designates the fact that the preparation of both the *m*-nitrobenzazido and the *m*-nitrophenyl isocyanate is given in reference (283) together with their utilization as reagents in the conversion of *p*-chlorophenol to the corresponding *N*-(*m*-nitrophenyl)carbamate. Of course, with commonly available reagents such extra citations need not be included.

In view of the nature and magnitude of the text of this book, there may be a tendency to regard it as a specialized Beilstein within its field. Such a characterization would carry the implication that the text comprises all known chemical information with respect to each component compound, whereas only the more important representatives of such data are offered. In this connection one common misunderstanding with respect to Beilstein's *Handbuch* has significance. The Beilstein classification employs the principle of "latest position in the system." This means that, when a given fact could logically be placed in several different places, it is in general associated with the last of such places in the systematic plan. For example, as the methyl ether of phenol, anisole could conceivably be discussed either under methyl alcohol or under phenol. Following the above principle, however, Beilstein discusses it under phenol with no mention whatever under methyl alcohol. For Beilstein's purpose this principle is extremely well founded, results in an orderly, systematic, and uniform procedure, and, if properly understood, causes no trouble to the user. Its employment does have the unfortunate result, however, that for compounds occurring early in the



systematic sequence the impression is often given to the uninitiated that nothing is known about reactions involving components themselves listed later in the classification scheme. In contrast to the above Beilstein usage, the present *Tables* are unrestricted by any such arbitrary rule. Inasmuch as a large proportion of the compounds with which it deals are those which in the Beilstein classification appear to be inadequately described because of their earlier position in the sequence, users will quickly appreciate the added convenience of a generous treatment of the chemistry involved.

#### *D. Preliminary tests*

For certain of the more common compounds included in these *Tables*, there exist specific or semi-specific color tests. These are generally simple to execute, may often be applied satisfactorily to minute amounts of material, and, when positive, are so significant that their trial, if indicated, should invariably precede the derivatization of the sample. Such tests are indicated by the symbol © but should be regarded as merely preliminary in character and not always carrying the same conviction as the derivatives.

#### *E. Derivatives*

The text section of each numbered compound is usually concluded by a group of derivatives. Those which for one reason or another have special importance are designated by the symbol © placed at the left-hand side of the page. Interspersed with such cases will frequently be found others not bearing this symbol but instead merely designated by a dash. Relatives of the original parent compound so designated comprise materials, knowledge of whose existence (or less commonly nonexistence) or properties may be needed for comparison with related cases for the particular parent or other isomers thereof. Wherever possible, specific data on each relative included in this derivative section are given; in many cases, however, where careful systematic search has failed to uncover any published record of the compound, it is characterized in these tables as "unreported." All chemists recognize that reliable information that a particular compound has not yet been reported is more to be desired than its complete omission; and this feature of this volume will effect substantial economies of time for its users. Naturally, as time goes by the constant publication of new data will enable some of these informational gaps to be filled.

More than one value for the melting point of a particular product derived from a numbered parent or, conversely, several citations for the same value will often be noted through all parts of this book. These practices serve, respectively, to suggest caution because of lack of agreement and to attract attention to the concordance of results of several different workers.

The sequence in which these derivatives are listed has no relation to their

respective merits as means of identification of the particular parent. For each class of compounds, the particular sequence is arbitrary but standard in form and sequence in order to facilitate intercomparison and easy reference. For any particular class, however, the sequence is similar to that employed in Order 1 for the corresponding nonchlorinated parent.

#### F. Literature references

The fifth and final section of the descriptive material comprising each serially numbered compound comprises the corresponding references to the chemical literature. These are associated with the corresponding portions of the descriptive text by arbitrary numbers set in bold-face carets, e.g. (5), the journal names being uniformly represented by the standard abbreviations employed by *Chemical Abstracts*. The single exception to the use of *Chemical Abstracts* abbreviations for literature references is that the German journal recently known as *Chemisches Zentralblatt* (but formerly as *Chemisches Centralblatt*) is here designated as *Cent.* This convention adequately suggests the name of the periodical in less space and improves the corresponding Beilstein abbreviation (C.) by avoiding confusion with Centigrade temperature.

The total number of such literature references in this book is very large, owing in part to the greatly increased scope of this Order 3 as compared with the restricted treatment of compounds of Order 1. It will be observed that, in addition to a much fuller record of the four fundamental physical constants, and a more generous regard for a diversified array of derivatives, this book (unlike its predecessor) deals extensively with the preparation and chemical behavior of its component species. Furthermore, whereas the earlier book arbitrarily excluded references to the patent literature, the present volume not only permits their inclusion but draws rather heavily upon it. The rapid growth of industrial organic chemistry, the fact that numerous chloro compounds of Order 3 represent individuals of great industrial significance, and the circumstances that for many such cases a large proportion of the available information is of such recent origin that little of it can be found in conventional monographs or other compendia have combined to necessitate considerable emphasis on the technical literature.

For a given individual numbered compound, a particular published article or patent is listed *only once*. The citation number representing the reference may be given many times in the descriptive text, but in the literature reference section the reference itself is not repeated. On the other hand, a given original article covering several individual compounds included in this book will be cited under each of the materials to which the article is relevant.

The order in which the literature references are arranged is determined by the sequence in which necessity for their mention arises in the text. This

results, of course, in what may appear to be a random sequence. The author is well aware that rearrangement of these references into a sequence comprising an alphabetical author index is possible. Such an operation, however, has been regarded as impracticable since it would multiply severalfold the opportunity for error and would be unlikely to confer advantages commensurate with the labor involved.

Literature references to journals considered to be generally accessible are given directly; but those to articles in journals with limited circulation or to articles in languages other than English, German, French, or Italian are usually accompanied by the location of the corresponding abstract in both the *Chemisches Centralblatt* and the *Chemical Abstracts*. This leads to the suggestion that users of this book, to whom a particular primary publication may be inaccessible, may themselves locate the corresponding abstracts by means of the usual Author Indexes to these works. Consultation of the abstract must never be regarded as equivalent to examination of the original publication but is generally better than no information at all.

Citations to original articles in scientific journals often refer to individual pages but sometimes also to a spread of pages, depending upon the nature of the article. The practice so frequently employed by others of citing an article merely by giving its initial page and leaving to the reader the often laborious job of locating the individual page germane to the aspect in question is deplored by the present author and has been avoided in this book. When a page spread (occasionally extending to the whole of a particular article) is cited, the reason is usually that the construction of the original paper is such that relevant material is scattered throughout the paper and individual page citation might be not only inadequate but even misleading. Since a given article appears (in general) but once in the group of literature references associated with each numbered compound, however, and since therefore the single number representing it may be used many times during the various aspects of the corresponding text, users finding that one of several individual pages so cited is inapplicable will recognize it is to be associated with some other aspect elsewhere in the text.

Attention is called to certain advantageous and unique practices followed by this book in connection with its citations of patents. The first element of patent citation is the name of the inventor (or of all, if more than one) if this information is known. The second element comprises the name of the company to which the patent has been assigned. All American patents are required by law to be issued to the inventors but are commonly assigned to the sponsor of the work. Foreign patents, however, do not always carry the names of individual inventors; in that event the company name has to serve both purposes. The third element is the nationality and number of the patent accompanied by its date of issue (not application). The fourth

element comprises reference to abstracts of the patent both in the *Chemisches Centralblatt* and in *Chemical Abstracts*. There are three reasons for this multiple form of abstract reference.

The first is that few chemists have immediate access to the corresponding original patents themselves and appreciate the convenience of the abstract. The second is the plain fact that the patent abstracts published by the *Chemisches Centralblatt* are usually so much more descriptive and more nearly complete than those of *Chemical Abstracts* that many chemists prefer to use the former. Doubters of this difference of quality between the two abstract journals are invited to convince themselves by direct comparison. Finally, the *Chemical Abstracts* reference is also included, however, because there may be some users of this book to whom the *Centralblatt* may not be available or who are timid about their ability to read even technical German. If in a particular case the patent has not been abstracted at all, this fact is also noted. Furthermore, because of the present inaccessibility of more recent issues of the *Centralblatt*, it has been necessary in some of the more recent references to cite only *Chemical Abstracts*.

In connection with the citation of patents, many instances will be noted in which the reference includes also the equivalent patents of other countries, each of these being accompanied by its dates, abstract references, etc., as for an individual patent.

The reader's attention is directed to the obvious fact that many patents are expressed in general terms so that, even though the protection sought may frequently cover one or more of the component compounds of this book, the specific individuals are not mentioned by name. No attempt has been made to interpret such general patents. For this reason systematic searchers will often consult higher or lower homologs of the compound comprising their initial interest.

## 6. Abbreviations

Necessity for economy of space has required in this book a continuation of the extensive set of abbreviations used with the earlier *Tables of Order 1* together with certain additions required by new circumstances. All these abbreviations have been selected so as to suggest the full word, particularly when assisted by the context. No attempt has been made to enslave the text to the abbreviations, however, and the full word is sometimes employed even though a mnemonic for it is given in the *Table of Abbreviations*.

## 7. Indexes

This book contains five different types of indexes; three of these are distinctly novel and two are conventional, as explained below.

### A. *The empirical formula index*

The index of empirical formulas lists each of the compounds in this book in the conventional familiar form under one or another of four parts according to whether the particular compound contains (1) only carbon and chlorine; (2) carbon, oxygen, and chlorine; (3) carbon, hydrogen, and chlorine; (4) carbon, hydrogen, oxygen, and chlorine. Within each of these parts the individual empirical formulas are arranged in groups according to increasing numbers of carbon atoms, and for a given number of carbon atoms according to increasing numbers of the other component atoms. Within each group of isomeric compounds the order of listing follows the sequence of the eight units comprising the Chemical Type Index (see below).

This empirical formula index contains also for each group of isomers both the molecular weight and the percentage chlorine content, each computed to one place of decimal units. This index not only serves as a convenient record of these constants but also suggests to the user isomers of the particular individual. The formula index may also be employed occasionally as a final verification of the presence or absence of a particular compound from the *Tables*, in possible instances where the names which occur to the worker do not appear in the alphabetical index.

A brief statistical analysis of this index may be of interest. The 1320 individual compounds comprising this book are distributed among 366 groups of isomers as follows:

	GROUPS OF ISOMERS	INDIVIDUALS
Part A C/Cl compounds	11	11
Part B C/O/Cl compounds	18	21
Part C C/H/Cl compounds	135	566
Part D C/H/O/Cl compounds	202	722
Total	366	1320

The minimum number of isomers for a given empirical formula is obviously one; 28 of the above 366 groups represent such minimum cases. The maximum possible number of individual compounds within a particular empirical formula is, of course, indeterminately large; however, it is of interest to note that, of the 366 groups of isomers in this book, the largest number of individual compounds (21) occurs for the empirical formula  $C_8H_7O_2Cl$ . Other formulas with substantial numbers of individuals comprise  $C_5H_9O_2Cl$  with 20,  $C_7H_{15}Cl$  and  $C_8H_{17}Cl$  each with 18,  $C_5H_{10}Cl_2$  with 17, and  $C_6H_{11}Cl$ ,  $C_6H_{13}Cl$ , and  $C_6H_9OCl$  each with 16, corresponding to a particular molecular weight.

### B. *Index of empirical formulas by percentage chlorine content*

This index lists the 366 empirical formulas of the numbered compounds contained in this book in order of diminishing percentage of chlorine. This

type of index is unique; nothing of this sort exists in any other publication so far as is known. Many uses of such an index will suggest themselves, the most obvious example being to suggest various empirical formulas corresponding to a particular chlorine content.

Within this index will be observed many examples of identical chlorine contents for several different formulas; e.g., a percentage chlorine of 37.5 is common to the four different formulas  $C_2H_3O_2Cl$ ,  $C_3H_7OCl$ ,  $C_8H_6OCl_2$ , and  $C_{14}H_9Cl_3$ , despite the fact (as seen from the Empirical Formula Index) that the molecular weights of the last two are quite different from the others.

### *C. Index of empirical formulas by molecular weights*

This index lists the 366 empirical formulas of the numbered compounds contained in this book in order of increasing magnitude of molecular weight. This index (like the preceding one) is unique, and nothing of the sort exists in any other publication so far as is known. Many uses of this index will suggest themselves, the most obvious example being to suggest various empirical formulas having the same molecular magnitude.

Within this index will also be observed many examples of identical molecular weights for several different formulas; e.g., the molecular weight of 136.6 is common to the three different formulas  $C_5H_9O_2Cl$ ,  $C_6H_{13}OCl$ , and  $C_8H_5Cl$ .

### *D. Index of compounds according to chemical types*

Since, as more fully explained earlier in this chapter, the component individuals of this book are not arranged in arbitrary genera and no standardized generic tests comparable to those of Order 1 have as yet been developed, the inclusion in this volume of an index in which the compounds are arranged according to the chemical classes to which they belong is of special value and utility.

In this chemical-type index, each compound is listed in at least one of eight chemical classes (units) as follows:

- Unit 1. Chloro substitution products of saturated acyclic hydrocarbons.
- Unit 2. Chloro substitution products of unsaturated acyclic hydrocarbons.
- Unit 3. Chloro substitution products of cyclic hydrocarbons.
- Unit 4. Chloro substitution products of hydroxy compounds (alcohols or phenols).
- Unit 5. Chloro substitution products (and their relatives) of carbonyl compounds (aldehydes, ketones, quinones, aldehyde polymers, acetals, alcoholates, etc.).
- Unit 6. Chloro substitution products of carboxylic acids and anhydrides.
- Unit 7. Acyl chlorides.
- Unit 8. Chlorine substitution products of ethers and of esters.

Compounds of the last five units containing more than one functional group are also listed under such of the others as may be appropriate. For example, 2,5-dichloro-3,6-dihydroxybenzoquinone-1,4 is listed both as a

carbonyl compound (Unit 6) and as a phenol (Unit 4); diethylene glycol mono(chloroacetate) is listed not only as an ester (Unit 8) but also as an alcohol (Unit 4) and an ether (Unit 8).

It may be of interest to summarize briefly the distribution of the compounds in this book among the several classes as shown in the following summary:

Unit 1	221	Unit 5	146
Unit 2	182	Unit 6	137
Unit 3	174	Unit 7	142
Unit 4	211	Unit 8	182

The total number of such unit listings (1395) thus exceeds the number of individual compounds (1320) by an amount representing the cases of multiple functions.

### *E. Alphabetical Index*

This conventional type of index includes not only the "principal" name, but also all the subsidiary names given in the *Tables* for every numbered compound in this book. It cannot, of course, guarantee to contain every name which might conceivably be applied since, for the field of chemistry, such names are legion. However, with every name that is listed is associated the corresponding location (or serial) number, so that use of this index is perfectly straightforward and the index requires no cross referencing within itself. The first letter of the first syllable of the name proper establishes its position in the alphabetical sequence irrespective of any literal or numerical prefixes such as *o-*, *m-*, *p-*, *sec-*, *ter-*, *cis-*, *trans-*,  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, *d-*, *l-*, *meso-*. Within a particular group of isomers with the same name, however, the sequence is *o-*, *m-*, *p-*; *sec-*, *ter-*; or  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, etc. *Iso* is not construed as a prefix but as part of the main root. Further details of this sort are given in the introduction to the index itself.

## CHAPTER II


### DIVISION A. SOLIDS

(3:0000-3:0499)

— PENTACHLOROACETONE  $\text{Cl}_2\text{CH}-\text{C}(\text{Cl})_2-\text{COCl}$   $\text{C}_2\text{HOC}_2\text{Cl}_5$  Beil. I - 656  
 $\text{I}_1-$   
 $\text{I}_2-$


M.P.  $+2.1^\circ$  B.P.  $192^\circ$

See 3:6205. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

— 2,5-DICHLOROTOLUENE   $\text{C}_7\text{H}_5\text{Cl}_2$  Beil. V - 296  
 $\text{V}_1-$   
 $\text{V}_2-$  (231)

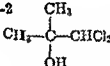
M.P.  $5^\circ$  B.P.  $199^\circ$  at 761 mm.  $D_{20}^{20} = 1.2535$

See 3:6245 Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

— *p*-CHLOROTOLUENE   $\text{C}_7\text{H}_7\text{Cl}$  Beil. V - 292  
 $\text{V}_1-$  (150)  
 $\text{V}_2-$  (226)


M.P.  $+7.8^\circ$  B.P.  $162^\circ$

See 3:8287. Division B: Liquids, Section 2,  $D_4^{20} < 1.15$ .

— 1,1-DICHLORO-2-METHYLPROPANOL-2   $\text{C}_4\text{H}_8\text{OCl}_2$  Beil. I - 382  
 (unsym.-Dichloro-ter-butyl alcohol;  
 dichloromethyl-methyl-carbinol)  $\text{I}_1-$   
 $\text{I}_2-$

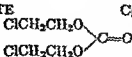
M.P.  $+8^\circ$  B.P.  $151^\circ$   $D_4^{19} = 1.2363$   $n_D^{19} = 1.4598$

See 3:5772 Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

— *o*-CHLOROPHENOL   $\text{C}_6\text{H}_5\text{OCl}$  Beil. VI - 183  
 $\text{VI}_1-$  (98)  
 $\text{VI}_2-$  (170)

M.P.  $8.0^\circ$  B.P.  $175-176^\circ$   $D_4^{25} = 1.2456$   $n_D^{25} = 1.5573$

See 3:5980. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

— DI-( $\beta$ -CHLOROETHYL) CARBONATE   $\text{C}_6\text{H}_{10}\text{O}_3\text{Cl}_2$  Beil. III -  
 $\text{III}_1-$   
 $\text{III}_2-$  (5)

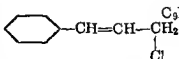
M.P.  $8.5^\circ$  B.P.  $240-241^\circ$   $D_4^{20} = 1.3506$   $n_D^{20} = 1.4616$

See 3:6790. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .



## 3:0010 CINNAMYL CHLORIDE

(3-Chloro-1-phenylpropene-1)


 Beil. V - 482  
 V<sub>1</sub>-(232)  
 V<sub>2</sub>-(372)

M.P.	B.P.				
8-9° (1)	140°	at 37 mm., sl. dec. (5)	$D_{25}^{25} = 1.08815$ (0)	$n_D^{25} = 1.58065$ (9)	
8° (2)	125-126°	at 22 mm. (6)	$D_4^{15} = 1.101$ (6)	$n_D^{15} = 1.587$ (8)	
7-8° (3)	120°	at 18 mm. (6)	$D_4^{12} = 1.000$ (8)		
4-9° (4)	117-110°	at 17 mm. (7)			
	118°	at 15 mm. (8)			
	115°	at 13 mm., sl. dec. (5)			
	110.5-120.5°	at 12 mm. (9)			
	116-117°	at 12 mm. (1)			
	108°	at 12 mm. (10)			
	106°	at 10 mm. (11)			
	109-110°	at 6 mm. (3)			
	102-103°	at 5 mm. (3)			
	101.5-103.4°	at 5 mm. (12)			
	94°	at 5 mm. (13)			
	86-87°	at 2 mm. (3)			

Care should be taken to avoid confusion of  $\bar{C}$  with the acid chloride of cinnamic acid; the acid chloride is properly designated as cinnamoyl chloride (3:0330); furthermore note that some of the older publications designate  $\bar{C}$  as "styryl chloride," which is now incorrect since in current usage the name *styryl* is reserved for the radical  $\text{C}_6\text{H}_5\text{CH}=\text{CH}-$  derived from styrene (14).

Attention is also taken to the fact (not fully recognized in the older work) that in some (but not all) reactions of  $\bar{C}$  the prods. obtained may in part be derived from the symionic mesomer of  $\bar{C}$ , viz., phenyl-vinyl-carbinyl chloride (3-chloro-3-phenylpropene-1); for examples see below.

$\bar{C}$  when pure is colorless oil with no odor of HCl; if HCl is present  $\bar{C}$  soon darkens on stdg. —  $\bar{C}$  should leave no residue on distillation, and best yields of  $\text{RMgCl}$  (see below) are obtainable only with freshly distilled  $\bar{C}$  (3).

[For prepn. of  $\bar{C}$  from cinnamyl alc. (1:5920) with HCl gas at 0° (yields: 92-93% (1), 78% (7), 60% (12)) (5) (6) (15), with HCl gas in  $\text{CCl}_4$  soln. at room temp. (85% yield (7)), with 6-7 wt. pts. 6 N HCl on distn. (79% yield (4)), or with conc. HCl +  $\text{ZnCl}_2$  in  $\text{C}_6\text{H}_6$  (54% yield (16) see indic. refs.; from cinnamyl alc. (1:5920) with  $\text{PCl}_3$  in  $\text{C}_6\text{H}_6$  (62.5% yield (1)), or  $\text{PCl}_3$  +  $\text{ZnCl}_2$  in  $\text{C}_6\text{H}_6$  (65% (16)) (note that  $\text{PCl}_5$  +  $\text{ZnCl}_2$  in  $\text{C}_6\text{H}_6$  gave only tar (16)); from cinnamyl alc. (1:5920) with  $\text{SOCl}_2$  + pyridine in  $\text{CHCl}_3$  (yields: 83% (3), 69-75% (12)), with  $\text{SOCl}_2$  + diethylaniline (18) or other tertiary bases (18), or with excess  $\text{SOCl}_2$  in  $\text{C}_6\text{H}_6$  (72% yield (16)) see indic. refs.; from cinnamyl ethers by cleavage with HCl (22° B<sub>6</sub>) on htg. under press. see (8); from cinnamyl acetate (see below) by passing in dry HCl see (18).]

[For prepn. of  $\bar{C}$  from phenyl-vinyl-carbinol [Beil. VI-572, VI<sub>1</sub>-(283)] (7) with HCl gas (7) (10) or with *p*-nitrobenzoyl chloride in ether on htg. in s.t. (10); from phenyl-vinyl-carbinyl acetate with HCl gas see (19).]

$\bar{C}$  with  $\text{Br}_2$  (1 mole) adds 2 atoms halogen yielding (20) (6) (10)  $\alpha,\beta$ -dibromo- $\gamma$ -chloro-*n*-propylbenzene, thls. from ether, m.p. 104-105° (6) (10).

$\bar{C}$  with conc. HI ( $D = 1.7$ ) (3 wt. pts.) in AcOH (7) or  $\bar{C}$  with KI in dry acetone (11) gives in good yield (7) cinnamyl iodide, pale yel. lfts., which after very careful recrystn. from AcOH have m.p. 57° (7); note, however, that the substance is very unstable, cf. (7) (11).

[ $\bar{C}$  on htg. with salts of acids yields a mixt. of the corresp. esters of cinnamyl alcohol (1:5920) and phenyl-vinyl-carbinol, the proportions of which vary with the nature of the acid radical, the metal, solvent, etc.; for extensive study of the reaction see (19) (7).] — [For behavior of  $\bar{C}$  with ethyl sodioacetoacetate (21), Ag salt of 3-hydroxynaphthoquinone-1,4 (2), or with 1,5-dichloroanthrone + aq. KOH (22) see indic. refs.]

$\bar{C}$  readily hydrolyzes to the corresp. alc. (1:5920): e.g.,  $\bar{C}$  with aq. on boilg. for 1 hr. is 75% saponified (7);  $\bar{C}$  with boilg. aq. 1 *N* NaOH is 95% hydrolyzed in 1 hr. (7); note, however, that  $\bar{C}$  is remarkably stable toward strong aq. alk. in cold (e.g., with 3.5 vols. 53% aq. NaOH only trace of hydrolysis even after 8 hrs. shaking (7)); note also that the cinnamyl alc. (1:5920) obtd. by hydrol. is contaminated with di-cinnamyl ether, h.p. 231–232°, and probably also by the ether from phenyl-vinyl-carbinol. —  $\bar{C}$  (10 g.) with excess cold dil. aq.  $\text{Na}_2\text{CO}_3$  on shaking 85 hrs. gives phenyl-vinyl-carbinol (1.3 g.) + cinnamyl alc. (1:5920) (0.7 g.), di-cinnamyl ether (2.6 g.) + unhydrolyzed chlorides (4.1 g.) (7).

[ $\bar{C}$  with abs. alc. KOH yields only (7) cinnamyl ethyl ether; note, however, that the course of the reaction is modified by pres. of aq. and that  $\bar{C}$  with NaOH in 70% aq. alc. the cinnamyl ethyl ether is accompanied by 25–30% of ethyl phenyl-vinyl-carbinyl ether (7); furthermore  $\bar{C}$  with silver oxide in abs. alc. (thus even in absence of aq.) gives both ethers (7) (for numerous details see (7)).]

[The behavior of  $\bar{C}$  with  $\text{NH}_3$  (or amines) is doubtless similarly influenced by the environment but has been less thoroughly studied. —  $\bar{C}$  in ether with large excess conc. aq.  $\text{NH}_4\text{OK}$  on stdg. gives (77% yield (23)) tetracinnamylammonium chloride, ndls. from alc., m.p. 199° (23);  $\bar{C}$  with abs. alc.  $\text{NH}_3$  gives (24) (25) (5) mono-, di- and tri-cinnamylamines.]

$\bar{C}$  with tertiary amines forms quaternary salts. e.g.,  $\bar{C}$  with  $\text{Me}_3\text{N}$  in abs. EtOH 24 hrs. at room temp. gives (26) (25) cinnamyl-trimethyl-ammonium chloride, very hygroscopic solid (for derivatives see (25) (26)); for quaternary salt formn. of  $\bar{C}$  with dimethylaniline (15) or pyridine (6) (5) see indic. refs.

[ $\bar{C}$  (1 mole) with aniline (4 moles) in ether as directed gives (50% yield (27)) *N*-(cinnamyl)-aniline, m.p. 21°, h.p. 200–202° at 12 mm., 178° at 3 mm. (27);  $\bar{C}$  (1 mole) with hexamethylenetetramine (1 mole) in aq. alc. as directed gives (20–30% yield (8)) cinnamaldehyde (1:0245).]

$\bar{C}$  (freshly distilled) with Mg in dry ether under special conditions gives (83% yield (31) (12)  $\text{RMgCl}$ : note carefully, however, that this Grignard is (or behaves as) a mixture consisting of 27% cinnamyl  $\text{MgCl}$ ,  $\text{C}_6\text{H}_5\text{—CH=CH.CH}_2\text{MgCl}$ , accompanied by 73% pheoyl-vinyl-carbinyl  $\text{MgCl}$ ,  $\text{C}_6\text{H}_5\text{—C(MgCl).CH=CH}_2$  (12).

[The reactns. of the Grignard mixture thus obtd. from  $\bar{C}$  therefore generally yield prods. corresponding to both the components sometimes accompanied by material originating from coupling reactns. of  $\text{RMgCl}$  (either or both types) with itself: e.g.,  $\text{RMgCl}$  (designating the above mixture) on acid hydrolysis with 3 *N*  $\text{H}_2\text{SO}_4$  gives not only both propenylbenzene [Beil. V-481,  $V_1$ -(231),  $V_2$ -(371)], b.p. 176°, and allylbenzene [Beil. V-484,  $V_1$ -(233),  $V_2$ -(373)], h.p. 156° (from the two  $\text{RMgCl}$  types) (combined yield 47% (12)), but also a high-boilg. residue (81% yield (12)) (from coupling of  $\text{RMgCl}$ , see below).]

[ $\bar{C}$  (2 moles) with Mg (1 atom wt.) in dry ether subsequently hydrolyzed gives a high-boilg. fracta. consisting of a solid and a liquid hydrocarbon: the solid hydrocarbon (8–9% yield (28)) (1) is 1,6-diphenylhexadiene-1,5 (dicinnamyl) [Beil.  $V_1$ -(338),  $V_2$ -(597)], lfts. from alc. or AcOH, m.p. 82° (1), 81–82° (29), h.p. 211° at 11 mm. (1), 180° at 5 mm. (29); the liquid hydrocarbon (42.9% yield (28)) has now been recognized (28) (contrary to earlier views (1)) as 1,4-diphenylhexadiene-1,5, b.p. 157–160° at 2 mm.,  $D_{20}^{20} = 0.9919$ ,  $n_D^{20} = 1.5890$  (28). — For mode of formation of these prods. see (28).]

[ $\bar{C}$  converted to  $\text{RMgCl}$  (see above) and reacted with  $\text{NH}_2\text{Cl}$  at  $-20^\circ$  gives (14% yield (33)) cinnamylamine.]

⑤ Phenyl-vinyl-acetic acid: cryst. from pet. ether at  $-10^{\circ}$ , m.p.  $23-24^{\circ}$  {30}. [From RMgCl with  $\text{CO}_2$  (note that ord. method gives low yields (38% {3} cf. {17}) but simple modification of carbonation technique raises yield to 62-66% {3}).] — This acid on htg. or on warming with either alk. or acid isomerizes (by change in position of double bond) to  $\alpha$ -phenylcrotonic acid (methylatropic acid) [Beil. IX-615] (see also next paragraph).

—  $\alpha$ -Phenylcrotonic acid (methylatropic acid): pr. from alc., ndls. or lfts. from aq., m.p.  $135-136^{\circ}$  {17} (*p*-nitrobenzyl ester, m.p.  $80-81^{\circ}$  {31}) (see also preceding paragraph). [From RMgCl (above) with ethyl chloroformate (3:7295) followed by hydrolysis of the intermediate ethyl phenyl-vinyl-acetate by htg. with 20% HCl or by shaking for 2 days with alkali (the hydrolysis being accompanied by simultaneous rearr. of the unsatd. linkage) {30}.]

⑥ Phenyl-vinyl-acetic anilide: cryst. from  $\text{C}_6\text{H}_6$ , alc., or  $\text{CHCl}_3$ , m.p.  $97-98^{\circ}$  {30}. [From RMgCl (above) with phenyl isocyanate in dry ether {30}; this prod. may be accompanied by a small amt. of  $\alpha$ -phenylcrotonanilide, m.p.  $192^{\circ}$ , from partial isomerization during the reactn. {30}.]

⑦ *N*-(Cinnamyl)phthalimide: cryst. from 90% alc. or 90% AcOH {24} or from *n*-PrOH {32}, m.p.  $156^{\circ}$  {32},  $153^{\circ}$  {24}. [From  $\bar{\text{C}}$  with K phthalimide by htg. at  $160^{\circ}$  for several hrs. {24}; note that the structure of this prod. has been confirmed as the cinnamyl (and not the phenyl-vinyl-carbinyl) type {32}.]

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# HEXACHLOROBUTENE-Y



Beil. S.N. 11

M.P.  $9.5-11^{\circ}$

B.P.  $125.5^{\circ}$  at 25 mm.

Sec 3:0050. Division C: Liquids with b.p. only at reduced pressure.

3:0013 7-CHLOROHEPTANOL-1  $\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{OH}$   $\text{C}_7\text{H}_{15}\text{OCl}$  Beil. S.N. 24  
( $\omega$ -Chloro-*n*-heptyl alcohol)  $\begin{array}{c} | \\ \text{Cl} \end{array}$

M.P.

B.P.

10-11° (1) (2) 150° at 20 mm. (1)  $D_4^{25} = 0.9098$  (1)  $n_D^{25} = 1.45367$  (1)  
120° at 13.5 mm. (3)

Cryst. from lt. pet.

[For prepn. of  $\bar{\text{C}}$  from  $\alpha,\omega$ -heptamethylene glycol (m p. 20.2° (3), 18° (1), b.p. 151° at 14 mm. (1), 146° at 9 mm. (3)) with conc. HCl as directed (yields: 65% (4), 46.2% (3), 43% (1)) see indie. refs.]

$\bar{\text{C}}$  with thiophenol in aq. NaOH lhd. 3 hrs. gives (1) 7-hydroxy-*n*-heptyl phenyl sulfide, ndls. from pet., m.p. 49°; this prod. with  $\text{SOCl}_2$  gives (1) 7-chloro-*n*-heptyl phenyl sulfide, brown oil (no const. reported.)

$\bar{\text{C}}$  (1 mole) with  $\text{Et}_2\text{NH}$  (3-4 moles) in a t. at 120-160° for 12-15 hrs gives (86% yield (3)) 7-(diethylamino)heptanol-1, b.p. 132° at 9.5 mm,  $D_4^{20} = 0.8681$ ,  $n_D^{20} = 1.4561$ , cf. (6); this prod. with  $\text{SOCl}_2$  in  $\text{C}_6\text{H}_6$  yields (3) (6) 7-(diethylamino)-*n*-heptyl chloride, b.p. 126° at 15 mm.,  $n_D^{25} = 1.4528$  (3) (corresp.  $\bar{\text{B}}$  HCl, m p. 82-84° (6))

$\bar{\text{C}}$  with morpholine gives (5) alm. quant 7-(4-morpholinyl)heptanol-1, b.p. 155.5-155.8° at 5 mm.,  $D_4^{25} = 0.9783$ ,  $n_D^{25} = 1.4747$  (corresp. *N*-phenylcarbamate, m.p. 71.0-72.0° cor.) (5). —  $\bar{\text{C}}$  (1 mole) with *N*-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (4) in alm. 100% yield (as salt) *N*-(7-hydroxy-*n*-heptyl)-*N'*-phenylpiperazine, m.p. 75.5-76.5° cor (corresp. *N*-phenylcarbamate, m p. 96.6-97.5° cor.).

$\bar{\text{C}}$  7-Chloro-*n*-heptyl *N*-phenylcarbamate: ndls. from pet. or dil. alc., m.p. 76-77° (3), 76° (1).

3:0013 (1) Bennett, Moses, *J. Chem. Soc.* 1931, 1659-1700 (2) Bennett, Reynolds, *J. Chem. Soc.* 1935, 139. (3) Altman, *Rec. trav. chim.* 57, 951-952 (1938). (4) Anderson, Pollard, *J. Am. Chem. Soc.* 61, 3439-3440 (1939). (5) Anderson, Pollard, *J. Am. Chem. Soc.* 61, 3440-3441 (1939). (6) Pyman, Levene (to Boot's Pure Drug Co.), Brit. 402,159, Dec. 21, 1933, *Cent.* 1934, 12005; *C.A.* 28, 3081 (1934).

3:0014 10-CHLORODECANOL-1  $\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{OH}$   $\text{C}_{10}\text{H}_{21}\text{OCl}$  Beil. I-420  
( $\omega$ -Chloro-*n*-decyl alcohol)  $\begin{array}{c} | \\ \text{Cl} \end{array}$  1<sub>r</sub>-(213)  
1<sub>r</sub>—

M.P.

B.P.

10-11° (1) 161-165° at 20 mm. (2)  $D_4^{25} = 0.9630$  (1)  $n_D^{25} = 1.45796$  (1)  
147.5-149° at 9 mm. (3)

Cryst. from pet. eth. (1). — Almost insol. aq.; eas. sol. alc., ether,  $\text{C}_6\text{H}_6$ , pet. ether.

[For prepn. of  $\bar{\text{C}}$  from  $\alpha,\omega$ -decamethylene glycol (Beil. 1-491, 1<sub>r</sub>-(256), 1<sub>r</sub>-(560)) (m p. 74.5° (1)) with conc. HCl (10 vol.) on boil. 4 hrs. (2) (3) (for improvements of this method see (1)) (yields: 65% (4), 50% (2)) see indie. refs.]

$\bar{\text{C}}$  on distn. with fused NaOH loses HCl giving two products regarded (2) as decamethylene oxide and decen-1-ol, but their structures have been questioned (3)]

$\bar{\text{C}}$  with thiophenol in aq. NaOH, heated 3 hrs., yields (1) 10-hydroxy-*n*-decyl phenyl sulfide, ndls. from lt. pet., m p. 66.5° (1); this prod. with  $\text{SOCl}_2$  gives 10-chloro-*n*-decyl phenyl sulfide, cryst. from alc., m p. 27.5° (1)

$\bar{\text{C}}$  with morpholine gives (5) alm. quant. 10-(4-morpholinyl)decanol-1, m p. 39.5-40.5°, b.p. 164.0-165.0° at 2 mm (corresp. *N*-( $\alpha$ -naphthyl)carbamate, m p. 66.5-67.5° cor. (5)).

—  $\bar{\text{C}}$  (1 mole) with *N*-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (5) in alm. 100%

formn. of  $\bar{C}$  from cetyl alc. +  $PCl_5$  (in pres. of mesityl oxide +  $Ac_2O$ ) (61.5% yield) see (10). — For formn. of  $\bar{C}$  from cetyl nle. with  $PCl_5$  see (5), but note that prod. always conts. unchanged cetyl alc. (1:5945) and cetene-1 (1:7000) (12) cf. (2).]

[For prepn. of  $\bar{C}$  from cetyl stearate (1:2193) with dry  $HCl$  gas (97% yield (11)), from cetyl acetate (1:2038) with dry  $HCl$  gas +  $ZnCl_2$  at  $180^\circ$  (13) see indic. refs.]

[For formn. of  $\bar{C}$  from a mixt. of  $K$  palmitate +  $K$  chloroacetate by electrolysis see (8).]

## PHYSICAL BEHAVIOR OF $\bar{C}$

[For study of electrophoretic mobility of emulsions of  $\bar{C}$  see (14).]

## CHEMICAL BEHAVIOR OF $\bar{C}$

### WITH INORGANIC REACTANTS

With metals. [ $\bar{C}$  with  $Li$  in dry ether under  $N_2$  gives (100% yield (15))  $C_{16}H_{33}Li$ ; on carbonation of mixt. with  $CO_2$  this is converted (51% yield (15)) to *n*-heptadecanoic acid (margaric acid) (1:0635): note, however, that  $\bar{C}$  with  $Li$  in pct. eth. (b.p.  $30-35^\circ$ ) gives (15) only 63% yield  $C_{16}H_{33}Li$  and this on carbonation only 27% overall yield of margaric acid accompanied by other prods. — For analogous reacts. of  $\bar{C}$  with  $Na$  see (15) (16); for react. of  $\bar{C}$  with  $Ca$  in dry ether under  $N_2$  see (15).]

$\bar{C}$  with  $Mg$  in dry ether + trace  $I_2$  gives in 6 hrs. (96% yield (1))  $C_{16}H_{33}MgCl$ .

With  $NH_3$ . [ $\bar{C}$  with liq.  $NH_3$  in alc. in s.t. at  $170^\circ$  for 24 hrs. gives (70% yield (17)) di-*n*-hexadecylamine, cryst. from alc., m.p.  $65^\circ$ , b.p.  $220^\circ$  at 3 mm. (17), accompanied by (24% yield (17)) *n*-hexadecylamine, m.p.  $45^\circ$ , b.p.  $146-148^\circ$  at 3 mm. ( $\bar{B}.HCl$ , lfts. from abs. alc., m.p.  $178^\circ$  (17)).]

With misc. inorg. reactants. [ $\bar{C}$  over spec. prepd.  $Al_2O_3$  at  $250^\circ$  loses  $HCl$  giving (94% yield (18)) of a mixt. of hexadecenes together with other prods.]

[ $\bar{C}$  with  $KOH$  at  $200-300^\circ$  gives (19) palmitic acid (1:0650);  $\bar{C}$  with alc.  $KSH$  gives (21) *n*-hexadecyl mercaptan;  $\bar{C}$  with nle.  $K_2S$  gives (21) di-*n*-hexadecyl sulfide.]

[ $\bar{C}$  with  $Na_2SO_3 \cdot 7H_2O$  (6 moles) at  $190-200^\circ$  for 8 hrs. under press. gives (98% yield (20)) sodium cetanesulfonate-1.]

[For study of rate of reactn. of  $\bar{C}$  with  $KI$  in acetone at  $50^\circ$  and  $60^\circ$  see (3).]

### WITH ORGANIC REACTANTS

[ $\bar{C}$  with nle.  $KOH$  gives (5) ethyl *n*-hexadecyl ether, f.p.  $19.9^\circ$  (5);  $\bar{C}$  with sodium allyl oxide refluxed 30 hrs. gives (70% yield (22)) allyl *n*-hexadecyl ether, pl. from aq. alc., m.p.  $25^\circ$  (22).]

[ $\bar{C}$  (1 mole) with 33% nle.  $MeNH_2$  (1 mole) in s.t. at  $140-150^\circ$  for 18 hrs. gives (68% yield (17)) *N*-methyl-di-*n*-hexadecylamine, ndls. from alc., m.p.  $36-37^\circ$ , b.p.  $269-271^\circ$  at 1 mm. (17) accompanied by (15% yield (17)) *N*-methyl-*n*-hexadecylamine, b.p.  $147-150^\circ$  at 1 mm. ( $\bar{B}.HCl$ , m.p.  $169-170^\circ$  (17)). —  $\bar{C}$  (1 mole) with  $Me_2NH$  (2 moles) in alc. in s.t. at  $140^\circ$  for 14 hrs. gives (82.5% yield (17)) *N,N*-dimethyl-*n*-hexadecylamine, b.p.  $158^\circ$  at 3 mm. ( $\bar{B}.HCl$ , lfts. from  $AcOEt$ /dioxane 5/1, m.p.  $198^\circ$  (17)).]

$\bar{C}$  with tertiary amines gives by addn. the corresp. quaternary ammonium salts [e.g.,  $\bar{C}$  with  $Me_3N$  (2 moles) in alc. in s.t. at  $100-105^\circ$  for 12-16 hrs. (17), or  $\bar{C}$  with  $Me_3N$  (1 mole) in closed bottle at  $110^\circ$  for 5 hrs. (7), gives (100% yield (17)) trimethyl-*n*-hexadecylammonium chloride, hygroscopic lfts. from  $AcOEt$ /alc., m.p. abt.  $70^\circ$  (17); for study of surface tension of aq. solns. of this salt see (7)].

$\bar{C}$  with pyridine (1 mole) in s.t. at  $110^\circ$  for 15 hrs. (23) or at  $120^\circ$  for 8 hrs. (7) gives *n*-hexadecyl-pyridinium chloride, cryst. with 1  $H_2O$  from alc./ether or  $C_6H_6$ , m.p.  $83^\circ$  (23),  $82^\circ$  (24) [for study of surface tension (7), conductivity (24), and elec. potential (24) of aq.

solns. of this salt see indic. refs.; for cat. hydrogenation of this salt to *N*-(*n*-hexadecyl) piperidine.HCl, m.p. 180° see (23); for study of favorable effect of press. on reactn. of  $\bar{C}$  with pyridine see (12)].

[For analogous reactn. of  $\bar{C}$  with *N,N*-dimethyl-benzylamine (17) or with isoquinoline (23) see indic. refs.]

[For reactn. of  $\bar{C}$  with  $\alpha$ -picoline + NaNH<sub>2</sub> yielding  $\alpha$ -(*n*-heptadecyl)pyridine, m.p. 23.5°, b.p. 206° at 2.5 mm.,  $\bar{B}.P.K.OH$ , m.p. 87°, or of  $\bar{C}$  with  $\gamma$ -picoline + NaNH<sub>2</sub> yielding  $\gamma$ -(*n*-heptadecyl)pyridine, m.p. 33°, b.p. 207-210° at 2.5 mm.,  $\bar{B}.P.K.OH$ , m.p. 115°, see (9)]

— *n*-Hexadecyl *p*-nitrobenzoate: m.p. 58.4° cor. (25). [Prepd. indirectly.]

— *n*-Hexadecyl 3,5-dinitrobenzoate: m.p. 66°. [Prepd. indirectly.]

— *N*-(*n*-Hexadecyl)phthalimide: unreported.

— *S*-(*n*-Hexadecyl)isothiouraea hydrochloride: m.p. 126-128° (26). [From  $\bar{C}$  with thiouraea in alc. on refluxing 3-4 days (26)]

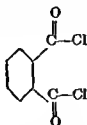
— *n*-Hexadecyl mercuric chloride: cryst. from pet. eth. or AcOEt, m.p. 114-115° (15). [Prepd. indirectly; note that m.p. of mixts. of this prod. with either  $n-C_{12}H_{25}HgCl$  (m.p. 114-114.5°) or  $C_{18}H_{37}HgCl$  (m.p. 115-116°) is depressed (15).]

3:0015 (1) Houben, Boedler, Fischer, *Ber* 69, 1768-1769; 1770-1780 (1936). (2) Clark, Streight, *Trans. Roy. Soc. Canada* (3) 23, III 77-89 (1929). (3) Conant, Hussey, *J. Am. Chem. Soc.* 47, 485 (1925). (4) Norris, Taylor, *J. Am. Chem. Soc.* 46, 756 (1924). (5) Phillips, Mumford, *J. Chem. Soc.* 1931, 1732-1735. (6) Tuttscheff, *Jahresber.* 1860, 406. (7) Hauser, Niles, *J. Phys. Chem.* 45, 954-959 (1940). (8) Matsui, Arakawa, *Mem. Coll. Sci. Kyoto Imp. Univ.* A-15, 189-194 (1932); *Cent.* 1932, II 2167; *C.A.* 26, 5264 (1932). (9) Tschitschibabin, *Bull. soc. chim.* (5) 5, 431-432 (1938). (10) Drake, Marvel, *J. Org. Chem.* 2, 394 (1937).

(11) Guyer, Bieler, Hardmeier, *Helv. Chim. Acta* 20, 1462-1467 (1937). (12) Fawcett, Gibson, *J. Chem. Soc.* 1934, 396-400. (13) Deutsche Hydrierwerke A.G., *Ger.* 567,014, Dec. 24, 1932; *Cent.* 1933, I 1015; *C.A.* 27, 1361 (1933). (14) Dickinson, *Trans. Faraday Soc.* 37, 140-148 (1941). (15) Meals, *J. Org. Chem.* 9, 211-218 (1944). (16) Morton, LeFevre, Hechenbleikner, *J. Am. Chem. Soc.* 58, 757 (1936). (17) Westphal, Jerchel, *Ber.* 73, 1006-1011 (1940). (18) Asinger, *Ber.* 75, 1254-1256 (1942). (19) Schrauth, *Ger.* 327,048, Oct. 4, 1920; *C.A.* 15, 2009 (1921). (20) Turkiewicz, St. Pilat, *Ber.* 71, 285 (1938).

(21) Fridau, *Ann.* 83, 16-20 (1852). (22) Davies, Heilbron, Givens, *J. Chem. Soc.* 1930, 2545. (23) Karrer, Kahnt, Epstein, Jaffe, Ishii, *Helv. Chim. Acta* 21, 233-236 (1938). (24) Lottermoser, Frotzcher, *Kolloid-Beihfte* 45, 305-307, 316, 320, 324, 340, 343 (1937). (25) Armstrong, Copenhagen, *J. Am. Chem. Soc.* 65, 2252-2253 (1943). (26) Sprague, Johnson, *J. Am. Chem. Soc.* 59, 1838-1839 (1937).

— *sym*-*o*-PHTHALYL DICHLORIDE



$C_6H_4O_2Cl_2$  Beil. IX - 805  
IX<sub>1</sub>-(363)

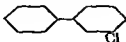
M.P. 16°

B.P. 276.7° at 760 mm.  $D_4^{20} = 1.4089$

$n_D^{20} = 1.5692$

See 3:6900. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

— 3-CHLOROBIPHENYL



$C_{12}H_9Cl$

Beil. V - 579

V<sub>1</sub>—  
V<sub>2</sub>-(483)

M.P. 16°

B.P. 284-285°

See 3:8940. Division B: Liquids, Section 2,  $D_4^{20} < 1.15$

formo. of  $\bar{C}$  from cetyl alc. +  $PCl_5$  (in pres. of mesityl oxide +  $Ac_2O$ ) (61.5% yield) see (10). — For formo. of  $\bar{C}$  from cetyl alc. with  $PCl_5$  see (5), but note that prod. always conts. unchanged cetyl alc. (1:5945) and cetene-1 (1:7000) (12) cf. (2).]

[For prepn. of  $\bar{C}$  from cetyl stearate (1:2193) with dry  $HCl$  gas (97% yield (11)), from cetyl acetate (1:2038) with dry  $HCl$  gas +  $ZnCl_2$  at  $180^\circ$  (13) see indic. refs.]

[For formn. of  $\bar{C}$  from a mixt. of  $K$  palmitate +  $K$  chloroacetate by electrolysis see (8).]

## PHYSICAL BEHAVIOR OF $\bar{C}$

[For study of electrophoretic mobility of emulsions of  $\bar{C}$  see (14).]

## CHEMICAL BEHAVIOR OF $\bar{C}$

### WITH INORGANIC REACTANTS

With metals. [ $\bar{C}$  with  $Li$  in dry ether under  $N_2$  gives (100% yield (15))  $C_{16}H_{33}Li$ ; on carbonation of mixt. with  $CO_2$  this is converted (51% yield (15)) to *n*-heptadecanoic acid (margaric acid) (1:0635): note, however, that  $\bar{C}$  with  $Li$  in pet. eth. (b.p.  $30-35^\circ$ ) gives (15) only 63% yield  $C_{16}H_{33}Li$  and this on carbonation only 27% overall yield of margaric acid accompanied by other prods. — For analogous reacts. of  $\bar{C}$  with  $Na$  see (15) (16); for react. of  $\bar{C}$  with  $Ca$  in dry ether under  $N_2$  see (15).]

$\bar{C}$  with  $Mg$  in dry ether + trace  $I_2$  gives in 6 hrs. (96% yield (1))  $C_{16}H_{33}MgCl$ .

With  $NH_3$ . [ $\bar{C}$  with liq.  $NH_3$  in alc. in s.t. at  $170^\circ$  for 24 hrs. gives (70% yield (17)) di-*n*-hexadecylamine, cryst. from alc., m.p.  $65^\circ$ , b.p.  $220^\circ$  at 3 mm. (17), accompanied by (24% yield (17)) *n*-hexadecylamine, m.p.  $45^\circ$ , b.p.  $146-148^\circ$  at 3 mm. ( $\bar{B}.HCl$ , lfts. from abs. alc., m.p.  $178^\circ$  (17)).]

With misc. inorg. reactants. [ $\bar{C}$  over spec. prepd.  $Al_2O_3$  at  $250^\circ$  loses  $HCl$  giving (94% yield (18)) of a mixt. of hexadecenes together with other prods.]

[ $\bar{C}$  with  $KSH$  gives (21)

(98% yield (20))

sodium octaethylsulfonate-1.]

[For study of rate of reactn. of  $\bar{C}$  with  $KI$  in acetone at  $50^\circ$  and  $60^\circ$  see (3).]

### WITH ORGANIC REACTANTS

[ $\bar{C}$  with alc.  $KOH$  gives (5) ethyl *n*-hexadecyl ether, f.p.  $19.9^\circ$  (5);  $\bar{C}$  with sodium allyl oxide refluxed 30 hrs. gives (70% yield (22)) allyl *n*-hexadecyl ether, pl. from aq. alc., m.p.  $25^\circ$  (22).]

[ $\bar{C}$  (1 mole) with 33% alc.  $MeNH_2$  (1 mole) in s.t. at  $140-150^\circ$  for 18 hrs. gives (68% yield (17)) *N*-methyl-di-*n*-hexadecylamine, ndls. from alc., m.p.  $36-37^\circ$ , h.p.  $269-271^\circ$  at 1 mm. (17) accompanied by (15% yield (17)) *N*-methyl-*n*-hexadecylamine, h.p.  $147-150^\circ$  at 1 mm. ( $\bar{B}.HCl$ , m.p.  $169-170^\circ$  (17)). —  $\bar{C}$  (1 mole) with  $Me_2NH$  (2 moles) in alc. in s.t. at  $140^\circ$  for 14 hrs. gives (82.5% yield (17)) *N,N*-dimethyl-*n*-hexadecylamine, b.p.  $158^\circ$  at 3 mm. ( $\bar{B}.HCl$ , lfts. from  $AcOEt$ /dioxane 5/1, m.p.  $198^\circ$  (17)).]

$\bar{C}$  with tertiary amines gives by addn. the corresp. quaternary ammonium salts [e.g.,  $\bar{C}$  with  $Me_3N$  (2 moles) in alc. in s.t. at  $100-105^\circ$  for 12-16 hrs. (17), or  $\bar{C}$  with  $Me_3N$  (1 mole) in closed hottle at  $110^\circ$  for 5 hrs. (7), gives (100% yield (17)) trimethyl-*n*-hexadecylammonium chloride, hygroscopic lfts. from  $AcOEt$ /alc., m.p. aht.  $70^\circ$  (17); for study of surface tension of aq. solns. of this salt see (7)].

$\bar{C}$  with pyridine (1 mole) in s.t. at  $110^\circ$  for 15 hrs. (23) or at  $120^\circ$  for 8 hrs. (7) gives *n*-hexadecyl-pyridinium chloride, cryst. with 1  $H_2O$  from alc./ether or  $C_6H_6$ , m.p.  $83^\circ$  (23),  $82^\circ$  (24) [for study of surface tension (7), conductivity (24), and elec. potential (24) of aq.

solns. of this salt see indic. refs.; for cat. hydrogenation of this salt to *N*-(*n*-hexadecyl) piperidine.HCl, m.p. 180° see (23); for study of favorable effect of press. on reactn. of  $\bar{C}$  with pyridine see (12)].

[For analogous reactn. of  $\bar{C}$  with *N,N*-dimethyl-benzylamine (17) or with isoquinoline (23) see indic. refs.]

[For reactn. of  $\bar{C}$  with  $\alpha$ -picoline + NaNH<sub>2</sub> yielding  $\alpha$ -(*n*-heptadecyl)pyridine, m.p. 23.5°, b.p. 206° at 2.5 mm.,  $\bar{B}$ .PhOH, m.p. 87°, or of  $\bar{C}$  with  $\gamma$ -picoline + NaNH<sub>2</sub> yielding  $\gamma$ -(*n*-heptadecyl)pyridine, m.p. 33°, h.p. 207-210° at 2.5 mm.,  $\bar{B}$ .PhOH, m.p. 115°, see (9).]

— *n*-Hexadecyl *p*-nitrobenzoate: m.p. 58.4° cor. (25) [Prepd. indirectly.]

— *n*-Hexadecyl 3,5-dinitrobenzoate: m.p. 66° [Prepd. indirectly.]

— *N*-(*n*-Hexadecyl)phthalimide: unreported.

— *S*-(*n*-Hexadecyl)isothioureia hydrochloride: m.p. 126-128° (26). [From  $\bar{C}$  with thioureia in alc. on refluxing 3-4 days (26)]

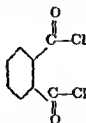
— *n*-Hexadecyl mercuric chloride: cryst. from pet. eth. or AcOEt, m.p. 114-115° (15). [Prepd. indirectly; note that m.p. of mixts. of this prod. with either *n*-C<sub>12</sub>H<sub>25</sub>HgCl (m.p. 114-114.5°) or C<sub>18</sub>H<sub>37</sub>HgCl (m.p. 115-116°) is depressed (15).]

3:0015 (1) Houben, Boedler, Fischer, *Ber.* 69, 1768-1769, 1779-1780 (1936). (2) Clark, Streight, *Trans. Roy. Soc. Canada* (3) 23, 111 77-89 (1929). (3) Coonant, Hussey, *J. Am. Chem. Soc.* 47, 485 (1925). (4) Norris, Taylor, *J. Am. Chem. Soc.* 46, 756 (1924). (5) Phillips, Mumford, *J. Chem. Soc.* 1931, 1732-1735. (6) Tuttschiff, *Jahresber.* 1860, 400. (7) Hauser, Niles, *J. Phys. Chem.* 45, 954-959 (1940). (8) Matsui, Arakawa, *Mem. Coll. Sci. Kyoto Imp. Univ. A-15*, 189-194 (1932); *Cent.* 1932, II 2167; *C.A.* 26, 5264 (1932). (9) Tschitschubabin, *Bull. soc. chim.* (5) 5, 431-432 (1938). (10) Drake, Marvel, *J. Org. Chem.* 2, 394 (1937).

(11) Guyer, Bieler, Hardmeier, *Helv. Chim. Acta* 20, 1462-1467 (1937). (12) Fawcett, Gibson, *J. Chem. Soc.* 1934, 390-400 (13) Deutsche Hydrierwerke A.G., *Ger.* 567,014, Dec. 24, 1932; *Cent.* 1933, I 1015; *C.A.* 27, 1301 (1933). (14) Dickinson, *Trans. Faraday Soc.* 37, 140-148 (1941). (15) Meals, *J. Org. Chem.* 9, 211-218 (1944). (16) Morton, LeFevre, Hechenbleikner, *J. Am. Chem. Soc.* 58, 757 (1936). (17) Westphal, Jerchel, *Ber.* 73, 1006-1011 (1940). (18) Asinger, *Ber.* 75, 1254-1256 (1942). (19) Schrauth, *Ger.* 327,048, Oct. 4, 1920; *C.A.* 15, 2009 (1921). (20) Turkiewicz, St. Pilat, *Ber.* 71, 285 (1938).

(21) Fridau, *Ann.* 83, 16-20 (1852). (22) Davies, Heilbron, Givens, *J. Chem. Soc.* 1930, 2545. (23) Karrer, Kahnt, Epstein, Jaffe, Ishii, *Helv. Chim. Acta* 21, 233-236 (1938). (24) Lottermoser, Frotscher, *Kolloid-Beihfte* 45, 305-307, 316, 320, 324, 340, 343 (1937). (25) Armstrong, Copenhaver, *J. Am. Chem. Soc.* 65, 2252-2253 (1943). (26) Sprague, Johnson, *J. Am. Chem. Soc.* 59, 1838-1839 (1937).

— *sym*-*o*-PHTHALYL DICHLORIDE



C<sub>8</sub>H<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub> Beil. IX - 805  
IX<sub>1</sub>-(363)

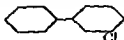
M.P. 16°

B.P. 276.7° at 760 mm.  $D_4^{20} = 1.4089$

$n_D^{20} = 1.5692$

See 3:6000. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

— 3-CHLOROBIPHENYL



C<sub>12</sub>H<sub>9</sub>Cl

Beil. V - 570

V<sub>1</sub>—

V<sub>2</sub>-(483)

M.P. 16°

B.P. 284-285°

See 3:8940. Division B: Liquids, Section 2,  $D_4^{20} < 1.15$ .



$\bar{C}$  is insol. aq.; sol. in alc. or ether.

[For prepn. from  $\alpha$ -chloroisovaleronitrile with conc. HCl at 100° see (1); from sodium isovalerate with aq. HOCl see (2).]

$\bar{C}$  with  $PCl_3$  yields (1)  $\alpha$ -chloroisovaleryl chloride (3:8144).

— Methyl  $\alpha$ -chloro-isovalerate: unreported.

— Ethyl  $\alpha$ -chloro-isovalerate: unreported.

—  $\alpha$ -Chloro-isovaleramide: unreported.

—  $\alpha$ -Chloro-isovaler-anilide: unreported.

—  $\alpha$ -Chloro-isovalero-*p*-toluidide: unreported.

3:0050 (1) Servais, *Rec. trav. chim.* 20, 51-53 (1901). (2) Schleich, *Ann.* 141, 323 (1867).

— 1,2,4-TRICHLOROBENZENE



$C_6H_3Cl_3$

Beil. V - 204

V<sub>1</sub>-(112)

V<sub>2</sub>-(156)

M.P. 17°

B.P. 213° cor.

See 3:6420. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

— *m*-CHLOROBENZALDEHYDE



$C_7H_5OCl$

Beil. VII - 234

VII<sub>1</sub>-(133)

M.P. 17°

B.P. 216°

$D_4^{20} = 1.2410$

$n_D^{20} = 1.5591$

See 3:6475. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

— 2,2,2-TRICHLOROETHANOL-1

$Cl_3C.CH_2OH$   $C_2H_3OCl_3$

Beil. I - 338

( $\beta,\beta,\beta$ -Trichloroethyl alcohol)

I<sub>1</sub>-(170)

I<sub>2</sub>-(337)

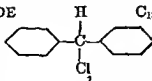
M.P. 17-18°

B.P. 161°

See 3:5775. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

3:0060 BENZOHYDRYL CHLORIDE

(Diphenylmethyl chloride,  
diphenylcarbinyl chloride,  
diphenyl-chloromethane,  
 $\alpha$ -chlorodiphenylmethane)



$C_{13}H_{11}Cl$

Beil. V - 590

V<sub>1</sub>-(278)

V<sub>2</sub>-(500)

M.P.

B.P.

[20.5° (1)]	190-191°	at 247 mm. (12)	$D_4^{19.3} = 1.1398$ (10)	$n_D^{19.5} = 1.5959$ (10)
18° (2)	173°	at 19 mm. (13) (14)		
17.6 (3)	169-170°	at 17 mm. (10)		
17-18° (4)	165°	at 17 mm. (15)		
17° (5)	167°	at 16 mm. (4)		
13-15° (6)	165.5°	at 15 mm. (1)		
14.5° (7)	161-162°	at 13 mm. (3)		
14° (8)	158.0-159.5°	at 12 mm. (1)		
(9) (24)	155-157°	at 12 mm. (16)		
13-14° (10)	156°	at 10 mm. (7)		

12-14° (11)	148-150°	at 6 mm.	(6)
	146.5-147.6°	at 6 mm.	(17)
	141°	at 4 mm.	(18)
	135-145°	at 4 mm.	(8)
	119-120°	at 2.5 mm.	(19)
	113-114°	at 1.5 mm.	(5)
	115-116°	at 1 mm.	(19)
	115°	at 1 mm.	(3)

$\bar{C}$  rapidly becomes turbid in contact with atmosphere and should be kept in sealed tubes (1). —  $\bar{C}$  on attempted distn. at ord. press. loses HCl and gives 1,1,2,2-tetraphenylethane [Beil. V-739, VI-(371)] (20), m p. 211°, and 1,1,2,2-tetraphenylethylene [Beil V-743, VI-(376)] (9), m.p. 227°.

[For prepn. of  $\bar{C}$  from diphenylcarbinol (1:5960) with dry HCl gas alone (9) (21), or in  $C_6H_6$  (92% yield (14)), or in  $C_6H_6 + CaCl_2$  (yield: 90% (1), 85% (3)) (11) (17), with  $SOCl_2$  in toluene (93.3% yield (2)), with  $PCl_5$  in  $POCl_3$  (92% yield (14)), or with  $BeCl_2$  (77% yield (8)) see indic. refs.; from diphenylmethane (1:7120) with  $PCl_5$  at 170° (together with other products) (22) or with  $NOCl$  (together with other products) (23) see indic. refs.: for formn. of  $\bar{C}$  from diphenylcarbinyl MgBr with  $C_6H_5N$  (42% yield + 8% diphenylacetone-trile + 5% 1,1,2,2-tetraphenylethane) see (10); from *bis*-(diphenylcarbinyl) ether in  $C_6H_6$  with HCl gas (77% yield) see (1); from diphenylcarbinylhydrazine with hoilg. dil. HCl see (24); from diphenyldiazomethane with HCl gas in ether at -80° see (25)]

[ $\bar{C}$  with molecular Ag in  $C_6H_6$  in absence of  $O_2$  gives 100% yield (19) of 1,1,2,2-tetraphenylethane (see first paragraph); in pres. of pure  $O_2$  yield drops to 2-8% and other products are formed (19);  $\bar{C}$  in  $C_6H_6$  refluxed some hours with Na gives (80-90% yield (14)) (9) (21) 1,1,2,2-tetraphenylethane (see first paragraph);  $\bar{C}$  with Na in liq.  $NH_3$  gives (26) 1,1,2,2-tetraphenylethane (65% yield) + diphenylmethane (1:7120) (27% yield).]

$\bar{C}$  in dry ether treated with Mg + trace of  $I_2$  immediately ppts. 1,1,2,2-tetraphenylethane whose yield may reach 95.5% (2); however, under special conditions (6)  $\bar{C}$  in ether with Mg + trace of  $I_2$  gives (51-71%) corresp.  $RMgCl$  cpd.; this prod. upon treatment with  $CO_2$  gives (yield: 84% (6), 32.5% (2)) diphenylacetic acid (1:0765), m p. 148°; the  $RMgCl$  cpd. does not react (2), however, with phenyl isocyanate.

[ $\bar{C}$  with pure  $AlCl_3$  immediately resinifies (11); however,  $\bar{C}$  in  $C_6H_6$  with  $AlCl_3$  gives (11) triphenyl-chloromethane (3:3410) + diphenylmethane (1:7120) with a very little triphenylmethane (1:7220).]

[ $\bar{C}$  htd. with 20% aq.  $Na_2SO_3$  soln. for 3 hrs. at 120° gives (100% yield (28)) (27) *bis*-(diphenylmethyl) ether [Beil. VI-679, VI-(326)], cryst. from alc., m p. 109° (27), 110° (17); note that this reaction probably results from intermediate diphenylcarbinol and that none of the expected sulfonate can be isolated.]

[For reactn. of  $\bar{C}$  with phenols +  $ZnCl_2$  yielding mono-, di- or tri-alkylated phenols according to conditions see (13) (29) cf. (30); for reactn. of  $\bar{C}$  with thiophenols see (31); for reactn. of  $\bar{C}$  with excess  $Br.Mg.C \equiv C.MgBr$  giving (40-50% yield) 1,1,4,4-tetraphenylbutine see (32); for reactn. of  $\bar{C}$  with anthrone +  $KOH$  see (33).]

$\bar{C}$  with aq. hydrolyzes yielding diphenylcarbinol (1:5960) or its reactn. products according to particular conditions; for extensive studies see (34) (12) (35) (18) (40) (35). —  $\bar{C}$  with EtOH undergoes alcoholysis yielding ethyl diphenylcarbinyl ether + HCl (for very extensive studies of this and related reactions see (1) (36) (4) (17) (37) (7) (35). —  $\bar{C}$  after warming with alc. may then be titrated quant. with stand. alkali using phenolphthalein (1).

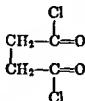
— Diphenylcarbinyl acetate [Beil. VI-680, VI-(326)]; cryst. from AcOH, m p. 40-41°.

[From  $\bar{C}$  with KOAc in AcOH (22).]

(19) Humnicki, *Roczniki Chem.* **11**, 670-673 (1931); *Cent.* 1931, II 3334. (20) Jusa, Riesz, *Mfonatsh.* **58**, 143 (1931).

(21) Cünther, Haller, Köster (to I.G.), Ger. 441,326, March 1, 1927; *Cent.* 1927, I 2358. (22) Farbwerke Meister Lucius & Brüning, Ger. 360,491, Oct. 3, 1922; *Cent.* 1923, II 479. (23) Chem. Fabrik. von Heyden, Ger. 365,212, Dec. 11, 1922; *Cent.* 1923, II 251. (24) Kaufmann, *Arch. Pharm.* **265**, 235-236 (1927).

— SUCCINYL (DI)CHLORIDE


 $\text{C}_4\text{H}_4\text{O}_2\text{Cl}_2$ 

Bell. II - 613

 II<sub>1</sub>-(264)

 II<sub>2</sub>-(553)

M.P. 20°

B.P. 103° at 760 mm.

 $D_4^{20} = 1.3748$ 
 $n_D^{20} = 1.4683$ 

See 3:6200. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

— METHYL *m*-CHLOROBENZOATE


 $\text{COOCH}_3$ ,  $\text{C}_8\text{H}_7\text{O}_2\text{Cl}$ 

Bell. IX-338

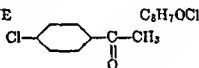
 IX<sub>1</sub>—

M.P. 20-21°

B.P. 231° at 763.5 mm.

See 3:6670. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

— *p*-CHLOROACETOPHENONE


 $\text{C}_8\text{H}_7\text{OCl}$ 

Bell. VII - 281

 VII<sub>1</sub>-(151)

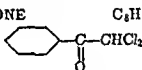
M.P. 20-21°

B.P. 232°

 $D_4^{20} = 1.188$ 

See 3:6735. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

—  $\omega,\omega$ -DICHLOROACETOPHENONE


 $\text{C}_8\text{H}_6\text{OCl}_2$ 

Bell. VII - 282

 VII<sub>1</sub>-(152)

M.P. 20°

B.P. 247-248°

See 3:6835. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

3:0000 *p*-CHLOROPHENETOLE  
(*p*-Chlorophenyl ethyl ether)


 $\text{OC}_2\text{H}_5$ ,  $\text{C}_8\text{H}_9\text{OCl}$ 

Bell. VI - 187

 VI<sub>1</sub>—

 VI<sub>2</sub>-(176)

M.P. 21° (1)

B.P. 211.6° cor. (3)

 $D_{20.2}^{20.2} = 1.12310$  (2)

 $n_D^{19} = 1.5227$  (5)

20.9° (2)

210-212° (1)(4)

20° (3)

Colorless oil, volatile with steam (6).

[For prepn. from *p*-chlorophenol (3:0475) +  $\text{C}_2\text{H}_5\text{I}$  in presence of KOH see (1), in presence of  $\text{K}_2\text{CO}_3$  + acetone (74% yield) see (4).]

$\bar{C}$  grad. added to 2 pts. conc.  $\text{HNO}_3$  ( $D = 1.485$ ) with cooling, then poured into aq., gives (6) 4-chloro-2-nitrophenetole [Beil VI-238], pale yel. ndls. from alc., m.p. 61° (6). [The mother liquor contains some 4-chloro-2,6-dinitrophenol [Beil. VI-260], m.p. 80° (6).]

$\bar{C}$  htd. at 100° with abt. 30 pts. of a soln. of const.-boilg. HBr (1 vol.) in AcOH (2 vols.) for 2 hrs. gave (4) 85% yield of *p*-chlorophenol (3:0475).

- ⑤ 5-Chloro-2-ethoxybenzenesulfonamide: cryst. from dil. alc., m.p. 134-134.5° u.c. (7). [From  $\bar{C}$  by treat. with chlorosulfonic ac. followed by conversion of the intermediate sulfonyl chloride to the sulfonamide by treatment with  $(NH_4)_2CO_3$  (71% yield (7))]. [Note that this prod. depresses the m.p. of the corresponding deriv. (m.p. 132-133° u.c.) from *o*-chlorophenetole (3-8735) (7) ]

3:0090 (1) Beilstein, Kurbatow, *Ann.* 176, 31 (1875). (2) Swarts, *J. chim. phys.* 20, 76 (1923). (3) Peratoner, Ortoleva, *Gazz. chim. ital.* 23, 1 226 (1893). (4) Borosel, *J. Am. Chem. Soc.* 53, 1408-1409 (1931). (5) Cotton, Mouton, *Ann. chim.* (8) 28, 216 (1913). (6) Reverdin, *During, Ber.* 32, 153 (1899). (7) Huntress, Carten, *J. Am. Chem. Soc.* 62, 603-604 (1940).

3:0095 1-CHLORO-OCTADECANE  $CH_3(CH_2)_{16}CH_2Cl$   $C_{18}H_{37}Cl$  Beil. S.N. 10  
(*n*-Octadecyl chloride;  
stearyl chloride)

M.P. 21° (1) B.P. 180-190° at 12 mm. (1) (2)  
18° (2)

Care must be taken to avoid confusion of  $\bar{C}$  with the acid chloride of stearic acid which is often designated as stearyl chloride (3-9960).

[For prepn. of  $\bar{C}$  from octadecanol-1 (stearyl alc.) (1:5953) with excess  $PCl_5$  on htg. (no statement of yields) (1) (10) or with  $PCl_5$  in  $SOCl_2$  (100% yield (10)) see indic. refs.]

[For study of heat of adsorption of  $\bar{C}$  on steel and its bearing on lubrication see (1); for study of electrophoretic mobility of emulsions of  $\bar{C}$  see (3) ]

$\bar{C}$  with Mg in dry ether yields (4)  $n-C_{18}H_{37}MgCl$  [this prod. with cyclopentanone (1:5446) gives (4) a tertiary alc. which on dehydration with  $KHSO_4$  yields (4) *n*-octadecylcyclopentene, b.p. 173-174° at 3 mm, m.p. 19°,  $D_4^{20} = 0.8462$ ; similarly  $C_{18}H_{37}MgCl$  with cyclohexanone (1:5465) gives (4) a tertiary alc. which with  $KHSO_4$  loses aq. giving (4) *n*-octadecylcyclohexene, b.p. 179-180° at 3 mm, m.p. 20°,  $D_4^{20} = 0.8458$ ].

[ $\bar{C}$  with  $C_6H_6 + AlCl_3$  undergoes Friedel-Crafts reactn. yielding (4) *n*-(7)-octadecylbenzene [Beil. V-473, V<sub>1</sub>-(361)], m.p. 25-26°, b.p. 180-181° at 3 mm.,  $D_4^{20} = 0.8566$ ,  $n_D^{20} = 1.4826$ .]

$\bar{C}$  (1 mole) with pyridine (1 mole) in s.t. at 110° for 15 hrs. gives (5) the corresp. quaternary salt, *N*-(*n*-octadecyl)pyridinium chloride, cryst. from alc./ether or  $C_6H_6$  as monohydrate, m.p. 82° (5), 86° (6); for study of conductivity and electric potential of latter see (6).

— *n*-Octadecyl *p*-nitrobenzoate: m.p. 64.3° cor. (7). [Prepd. indirectly.]

— *n*-Octadecyl 3,5-dinitrobenzoate: unreported.

— *N*-(*n*-Octadecyl)phthalimide: unreported.

— *S*-(*n*-Octadecyl)isothiourea: m.p. 83-85° (8). [Prepd. indirectly.]

— *n*-Octadecyl mercuric chloride: m.p. 115-116° (9). [Prepd. indirectly: note that m.p. of this prod. either with  $C_{18}H_{37}HgCl$  (m.p. 114-115°) or with  $C_{18}H_{37}HgBr$  (m.p. 110-111°) is depressed (9).]

3:0095 (1) Frewing, *Proc. Roy. Soc. (London)* A-182, 270-286 (1944). (2) Meyer, Streuli, *Hds. Chim. Acta* 20, 1179-1183 (1937). (3) Dickinson, *Trans. Faraday Soc.* 37, 140-148 (1941). (4) Suida, Gemasner, *Ber.* 72, 1165-1173 (1939). (5) Karrer, Kahnt, Epstein, Jaffe, Ishii, *Hds. Chim. Acta* 21, 231-234 (1934). (6) Lottermoer, Frotscher, *Kolloid-Beihfte* 45, 305-306, 320-321, 325, 341 (1937). (7) Armstrong, Copenhaver, *J. Am. Chem. Soc.* 63, 2252-2253 (1943). (8) Snell, Weissberger, *J. Am. Chem. Soc.* 61, 453 (1939). (9) Meals, *J. Org. Chem.* 9, 213-217 (1944). (10) Davies, Heilbron, Owens, *J. Chem. Soc.* 1930, 2516.

— *n*-OCTADECANOYL CHLORIDE  $\text{C}_{18}\text{H}_{35}\text{OCl}$  Beil. II - 384  
 (Stearoyl chloride)  $\text{CH}_3(\text{CH}_2)_{16}-\text{C}(=\text{O})\text{Cl}$  II<sub>1</sub>-(176)  
 II<sub>2</sub>-(360)  
 M.P. 23-24° B.P. 215° at 15 mm.

See 3:9960. Division C: Liquids with b.p. reported only at reduced pressure.

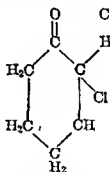
3:0100 1-CHLOROHEPTADECANE  $\text{CH}_3(\text{CH}_2)_{15}\text{CH}_2\text{Cl}$   $\text{C}_{17}\text{H}_{35}\text{Cl}$  Beil. I —  
 (*n*-Heptadecyl chloride) I<sub>1</sub>-(69)  
 I<sub>2</sub>—  
 M.P. 24° (1) B.P. 192-195° at 10 mm. (1)

[For prepn. of  $\bar{\text{C}}$  from *N*-benzoylheptadecylamine (*N*-(*n*-heptadecyl)benzamide) with  $\text{PCl}_5$  on distn. (50% yield) see (1); from silver stearate (or other stearates of metals of 1st, 2nd, or 3rd group) with  $\text{Cl}_2$  see (2).]

- *n*-Heptadecyl *p*-nitrobenzoate: m.p. 53.8° cor. (3). [Prepd. indirectly.]
- *n*-Heptadecyl 3,5-dinitrobenzoate: unreported.
- *N*-(*n*-Heptadecyl)phthalimide: unreported.
- *S*-(*n*-Heptadecyl)isothioureia picrate: unreported.
- *n*-Heptadecyl mercuric chloride: unreported.

3:0100 (1) von Braun, Sobacki, *Ber.* 44, 1473 (1911). (2) C. Hunsdiecker, H. Hunsdiecker, E. Vogt, U.S. 2,176,181, Oct. 17, 1939; *C.A.* 34, 1680 (1940); *Brit.* 455,505, Dec. 10, 1936; *Cent.* 1937, I 2258; *C.A.*, 31, 2233 (1937); *French* 803,941, Oct. 12, 1936; *Cent.* 1937, I 2258; [*C.A.* 31, 2616 (1937)]. (3) Armstrong, Copenhagen, *J. Am. Chem. Soc.* 65, 2252-2253 (1943).

3:0120 2-CHLOROCYCLOHEXANONE-1  $\text{C}_6\text{H}_9\text{OCl}$  Bell. VII - 10  
 VII<sub>1</sub>-(8)



M.P.	B.P.		
24° (1)	90-91° at 14-15 mm. (19)	$D_{15}^{20} = 1.161$ (6)	$n_D^{20} = 1.4825$ (6)
23-24° (2)	88-90° at 16 mm. (5)		
23.2° cor. (19)	82-85° at 14 mm. (8)		
23° (3) (4) (5)	82° at 13 mm. (4)		
22-23° (6) (7)	82-83° at 10 mm. (3)		
	80.5° at 11 mm. (5)		
	79° at 7 mm. (6)		

$\bar{\text{C}}$  has very disagreeable physiological effects; breathing of its ether solutions or exposure of skin to its vapor produces violent illness and temporary complete blindness; also produces an eczema on the hands (although sensitivity of individuals varies) (9). —  $\bar{\text{C}}$  dec. slightly on distn. even in vacuo (10).

[For prepn. from cyclohexanone (1:5455) with  $\text{Cl}_2 + \text{H}_2\text{O}$  (61-66% yield (19)), by actn. of  $\text{Cl}_2 + \text{CaCO}_3 + \text{H}_2\text{O}$  ( $\text{HOCl}$ ) (50-60% yield (7) (8)) see (7) (8) (10) (3) (4); by direct



## — 3,5-DICHLOROTOLUENE

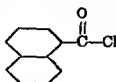
 $C_7H_5Cl_2$ 

Beil. V - 296

V<sub>1</sub>—V<sub>2</sub>—

M.P. 26°

B.P. 201-202° cor. at 760 mm.

See 3:6310. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .—  $\alpha$ -NAPHTHOYL CHLORIDE $C_{11}H_7OCl$ 

Beil. IX - 048

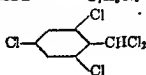
IX<sub>1</sub>-(275)

M.P. 26°

B.P. 297.5°

See 3:6930. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .3: 0142 2,4,6-TRICHLOROBENZAL (DI)CHLORIDE  
(2,4,6-Trichlorobenzylidene (di)chloride) $C_7H_2Cl_5$ 

Beil. S.N. 466



M.P. 27° (1)

B.P. 158° at 15 mm. (1)

Cryst. from MeOH

[For prepn. of  $\bar{C}$  from 2,4,6-trichlorotoluene (3:0380) with  $Cl_2$  at 200° (82% yield) see (1).] $\bar{C}$  on hydrolysis with fuming  $H_2SO_4$  gives (94% yield (1)) 2,4,6-trichlorobenzaldehyde (3:1200).

3:0142 (1) Lock, Ber. 66, 1532 (1933).

3: 0150 2,6-DICHLORO-3-METHYLPHENOL  
(2,6-Dichloro-*m*-cresol) $C_7H_5OCl_2$ 

Beil. VI —

VI<sub>1</sub>—VI<sub>2</sub>-(356)

M.P. 27° (1)

B.P. 240.5-242.5°

(1)

239.5-240.5° at 745 mm. (2)

80-85° at 4 mm. (2)

[For prepn. of  $\bar{C}$  from 4-amino-2,6-dichloro-3-methylphenol (1) via diazotization and treatment with alk.  $SnCl_2$  (very poor yield) see (1); from 3-methylphenol-2,6-disulfonic acid (1) or from 3-methylphenolsulfonic acid-6 in nitrobenzene (2) with  $Cl_2$  see indic. refs.; from 2-chloro-3-methylphenol (3:1055) or from 6-chloro-3-methylphenol (3:0700) in cold  $CHCl_3$  with 1 mole  $Cl_2$  see (1); from *m*-cresol (1:1730) in  $CHCl_3$  at 0° with  $Cl_2$  (other products are also formed) see (1).]


 $\bar{C}$  in  $CHCl_3$  with 1 mole  $Cl_2$  gives alm. quant. yield (1) 2,4,6-trichloro-*m*-cresol (3:0618), m.p. 46° (1). $\bar{C}$  in  $CHCl_3$  with 1 mole  $Br_2$  yields (2) 2,6-dichloro-4-bromo-3-methylphenol, m.p. 64-65° (2).

① 2,6-Dichloro-3-methylphenyl benzoate: clusters of small prismatic pl. from alc., m.p. 90.5° (1). [From  $\bar{C}$  with benzoyl chloride in pyridine (1).]

② 2,6-Dichloro-3-methylphenyl benzenesulfonate: thin lustrous pl. from alc., m.p. 70° (1). [From  $\bar{C}$  with benzenesulfonyl chloride in pyridine (1).] [Note proximity of the m.p. of this deriv. to that of the corresp. deriv. of 2,4-dichloro-3-methylphenol (3:1205).]

③ 2,6-Dichloro-3-methylphenyl *p*-toluenesulfonate: small pr. from alc., m.p. 92-92.5° (1). [From  $\bar{C}$  with *p*-toluenesulfonyl chloride in pyridine (1).]

3:0150 (1) Huston, Chen, *J. Am. Chem. Soc.* 55, 4217-4218 (1933). (2) Huston, Neely, *J. Am. Chem. Soc.* 57, 2178 (1935).

3:0158 2-CHLORO-3,4-DIMETHYLPHENOL   $C_6H_5OCl$  Beil, SN. 529  
(3-Chloro-*o*-4-xenol)

M.P. 27° (1)

Cryst. from lt. pet.


[For prepn. of  $\bar{C}$  from 2-amino-3,4-dimethylphenol (3-amino-*o*-4-xenol) (1) via diazotization and use of  $Cu_2Cl_2$  reaction (yield not stated) see (1).]

The nitration of  $\bar{C}$  has not been reported, and neither of the two possible mononitro-derivs. nor the corresp. dimtro-deriv. is known.

— 2-Chloro-3,4-dimethylphenyl acetate: unreported.

④ 2-Chloro-3,4-dimethylphenyl benzoate: m.p. 87° (1).

3:0159 (1) Hinkel, Ayling, Bevan, *J. Chem. Soc.*, 1923, 2531.

3:0165  $\beta$ -PHENOXYETHYL CHLORIDE   $C_6H_5OCl$  Beil, VI - 142  
( $\beta$ -Chloroethyl phenyl ether,  $VI_1$ -(81)  
*o*-chlorophenetole)  $O.CH_2CH_2Cl$   $VI_2$ -(144)

M.P. 25° (1) (2)	B.P. 217-220° at 760 mm. (1) (4)
28° (5) (4) (3)	221° at 754 mm. (2)
	220° (6)
	122.3° at 26 mm. (7)
	103-104° at 12 mm. (8)
	100-102° at 12 mm. (5)

Insol. aq., very eas. sol. alc., ether,  $C_6H_6$ , lgr.

[For prepn. from  $\beta$ -phenoxyethyl alcohol (1.6518) +  $SOCl_2$  + pyridine (88% yield (7)) see (7) (1); from sodium phenolate + ethylene dichloride (3:5130) (poor yield) see (5) (3); from ethylene chlorobromide see (6) (1)].

$\bar{C}$  +  $AlCl_3$  + phthalic anhydride in  $CS_2$  yields (9) *o*-[4(?)-( $\beta$ -chloroethyl)-benzoyl]-benzoic ac., cryst. from  $C_6H_6$ , m.p. 145° (9).

⑤ *N*-( $\beta$ -Phenoxyethyl)tetrachlorophthalimide: rods from acetone, m.p. 155-156° (10)  
[From  $\bar{C}$  with K tetrachlorophthalimide (10).]

3:0165 (1) Jones, *J. Chem. Soc.* 1936, 1861. (2) Henry, *Compt. rend.* 96, 1233 (1883). (3) Clemo, Perkin, *J. Chem. Soc.* 121, 644-645 (1922). (4) Butler, Relfreew, Cretcher, Souther, *J. Am. Chem. Soc.* 59, 229 (1937). (5) Wohl, Berthold, *Ber.* 43, 2179 (1910). (6) Bentley, Haworth, Perkin, *J. Chem. Soc.* 69, 165 (1896). (7) Kirner, *J. Am. Chem. Soc.* 48, 2748 (1926). (8) Földi, *Ber.* 53, 1845 (1920). (9) Bruson, Eastes, *J. Am. Chem. Soc.* 60, 2504 (1938). (10) Allen, Nicholls, *J. Am. Chem. Soc.* 56, 1409-1410 (1934).



3:0170 9-CHLORONONANOL-1  $\text{CH}_2(\text{CH}_2)_7\text{CH}_2\text{OH}$   $\text{C}_9\text{H}_{19}\text{OCl}$  Beil. S.N. 24  
 ( $\omega$ -Chloro-*n*-nonyl alcohol)  $\begin{array}{c} | \\ \text{Cl} \end{array}$

M.P. 28° (1) B.P. 140-145° at 20 mm. (1)  
 146.5° at 14 mm. (2)

Cryst. from lt. pet.

[For prepn. of  $\bar{\text{C}}$  from  $\alpha,\omega$ -nonamethylene glycol [Beil. I<sub>2</sub>-(558)] (m.p. 46° (1)) with conc. HCl as directed (yields: 90% (1), 86% (2), 65% (3)) see indic. refs.]

$\bar{\text{C}}$  with thiophenol in aq. NaOH htd. 3 hrs. gives (1) 9-hydroxy-*n*-nonyl phenyl sulfide, cryst. from lt. pet., m.p. 60°. [This prod. with  $\text{SOCl}_2$  gives (1) 9-chloro-*n*-nonyl phenyl sulfide, cryst. from nq. alc. at low temp., m.p. 5° (1).]

$\bar{\text{C}}$  (1 mole) with  $\text{Et}_2\text{NH}$  (3-4 moles) in s.t. at 120-160° for 12-15 hrs. gives (90% yield (2)) 9-(diethylamino)nonanol-1, b.p. 161.5° at 12 mm.,  $D_4^{25.4} = 0.8635$ ,  $n_D^{20} = 1.4574$  (2), cf. (5); this prod. with  $\text{SOCl}_2$  in  $\text{C}_6\text{H}_6$  gives (2) (5) 9-(diethylamino)-*n*-nonyl chloride, b.p. 145° at 10 mm.,  $n_D^{17.4} = 1.4535$  (2) (corresp.  $\bar{\text{B}}\cdot\text{HCl}$ , m.p. 85-86° (5)).]

$\bar{\text{C}}$  with morpholino gives (4) alm. quant. 9-(4-morpholinyl)nonanol-1, m.p. 31°, b.p. 173.0-173.5° at 5 mm. (corresp. *N*-( $\alpha$ -naphthyl)carbamate, m.p. 54.0-56.0° cor.). —  $\bar{\text{C}}$  (1 mole) with *N*-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (3) in alm. 100% yield (as salt) *N*-(9-hydroxy-*n*-nonyl)-*N'*-phenylpiperazine, m.p. 80.0-80.5° cor. (corresp. *N*-phenylcarbamate, m.p. 94.0-95.0° cor.).

① 9-Chloro-*n*-nonyl *N*-phenylcarbamate: cryst. from dil. alc., m.p. 70.0-70.5° (3), 67° (1) (2).

② 9-Chloro-*n*-nonyl *N*-(*m*-nitrophenyl)carbamate: m.p. 57° (2).

3:0170 (1) Bennett, Mosses, *J. Chem. Soc.* 1031, 1697-1701. (2) Altman, *Rec. trav. chim.* 57, 951-952 (1938). (3) Anderson, Pollard, *J. Am. Chem. Soc.* 61, 3430-3440 (1939). (1) Anderson, Pollard, *J. Am. Chem. Soc.* 61, 3440-3441 (1939). (5) Pyman, Levene (to Boot's Pure Drug Co.), Brit. 402,159, Dec. 21, 1933; *Cent.* 1934, I 2005; *C.A.* 28, 3081 (1934).

3:0172 12-CHLORODODECANOL-1  $\text{C}_{12}\text{H}_{25}\text{OCl}$  Beil. S.N. 24  
 ( $\omega$ -Chloro-*n*-dodecyl alcohol;  $\omega$ -chlorolauryl alcohol)  $\text{CH}_2(\text{CH}_2)_{10}\text{CH}_2\text{OH}$   
 $\begin{array}{c} | \\ \text{Cl} \end{array}$

M.P. 28° (1) B.P. 134° at 1 mm. (1)

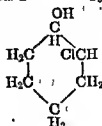
Colorless cryst. from lt. pet.

[For prepn. of  $\bar{\text{C}}$  from  $\alpha,\omega$ -dodecanmethyleno glycol [Beil. I<sub>2</sub>-(562)] (m.p. 83.5-84.5° (1)) with conc. HCl on litg. as directed (50% yield crude prod.) see (1).]

① 12-Chlorododecyl *N*-phenylcarbamate: ndls. from pet., m.p. 66° (1).

3:0172 (1) Bennett, Gudgcon, *J. Chem. Soc.* 1938, 1679-1681.

3:0175 *trans*-2-CHLOROCYCLOHEKANOL-1  $\text{C}_6\text{H}_{11}\text{OCl}$  Beil. VI - 7  
 (*trans*-Cyclohexeno chlorohydrin)  $\text{VI}_1$ —  
 $\text{VI}_2$ -(12)



M.P.	B.P.			
29° (1) (2)	104–100° at 45 mm. (4)	$D_{25}^{35} = 1.1233$ (3)	$n_D^{35} = 1.4832$ (3)	
27° (3)	93° at 26 mm. (3)			
	88–90° at 20 mm. (4)	$D_{25}^{16} = 1.146$ (1)	$n_D^{16} = 1.4850$ (1)	
	85–86° at 17 mm. (26)			
	84–85° at 16 mm. (2) (7)			
	87° at 15 mm. (1)			
	92° at 10 mm. (5)			

[See also *cis*-2-chlorocyclohexanol-1 (3:9374).]

Both the two theoretically possible geometrical stereoisomers of 2-chlorocyclohexanol-1 are known. The single form obtained from cyclohexene (tetrahydrobenzene) by addn. of HOCl or from cyclohexene oxide by addn. of HCl is now regarded (3) as the *trans* isomer  $\bar{C}$ . The *cis* form (3:9374) is obt'd. by other methods.

Colorless pr. from mixt. of  $C_6H_6$  + lgr. at low temp.;  $\bar{C}$  has characteristic odor, is vol. with steam.

[For prepn. of  $\bar{C}$  from cyclohexene (tetrahydrobenzene) (1:8070) with HOCl (yields: 70–73% (4), 70% (5)) (6) (7) (8) or with *N*-chlorourea (yield: 74% (26), 54% (9)) see indic. refs.; from cyclohexene oxide (see below) with conc. HCl or with  $ZnCl_2$  in dry ether see (3); for probable formn. of  $\bar{C}$  from cyclohexene (1:8070) with EtOCl (3:7022) see (10); for formn. of a mixt. of both stereoisomeric 2-chlorocyclohexanols contg. 27–28%  $\bar{C}$  + 72–73% *cis*-isomer from 2-chlorocyclohexanone (3:0120) by reductn. with isopropyl MgCl, *ter*-butyl MgX, or cyclohexyl MgX see (3); for formn. of a mixt. (b.p. 78–80° at 12 mm.) of both isomers by hydrolysis of 2-chlorocyclohexanyl acetate see (11).]

$\bar{C}$  with aq. NaOH at room temp. gives (yields. 70–73% (12), 70–75% (5), 80% (9), 55% (13)) cyclohexene oxide (1,2-epoxycyclohexane) [Beil. XVII-21], b.p. 131.5° at 760 mm. [Note that reactn. of  $\bar{C}$  with alk. is 300 times as fast as that of the *cis* isomer (3:9374) (use in detn. of proportion of  $\bar{C}$  in mixts. of isomers), that the latter with alk. gives no epoxy cpd. but instead cyclohexanone, and finally that  $\bar{C}$  can be separated from its isomer by conversion to cyclohexene oxide from which the remaining *cis* isomer can be sep'd. by distn. (3).]

$\bar{C}$  with alk. or with aq. KCl is *not* converted to *cis* isomer (3) but  $\bar{C}$  on protracted htg. with HCl rearr. to a small extent to the *cis* isomer.

[For use of  $\bar{C}$  as seed disinfectant see (15).]

The halogen atom of  $\bar{C}$  is fairly reactive, but its replacement often involves rearr. of the cyclohexyl ring to a cyclopentyl ring.

$\bar{C}$  on hoilg. with dil. alc. slowly gives (1) *trans*-cyclohexanediol-1,2 [Beil. VI-740] with cyclopentylformaldehyde (formylcyclopentane), the latter increasing in pres. of dil.  $H_2SO_4$  or of  $CaCl_2$  (1).]

$\bar{C}$  with NaOMe in MeOH yields (14) *cis*-2-methoxycyclohexanol-1 [Beil. VI-740], b.p. 181.5° at 760 mm.,  $D_{25}^{20} = 1.015$ ,  $n_D^{20} = 1.4605$  (14);  $\bar{C}$  with NaOEt in EtOH (14) (or  $\bar{C}$  in EtOH treated with Na in attempted reductn. (16) gives (87% yield (16)) *cis*-2-ethoxycyclohexanol-1 [Beil. VI-740], b.p. 187° at 760 mm.,  $D_{25}^{20} = 0.982$ ,  $n_D^{20} = 1.4563$  (14);  $\bar{C}$  with sodium *n*-propylate yields (14) 2-*n*-propoxycyclohexanol, b.p. 205° at 760 mm.,  $D_{25}^{20} = 0.970$ ,  $n_D^{20} = 1.4580$  (14);  $\bar{C}$  with sodium cyclohexanolate yields (14) 2-cyclohexanocyclohexanol, m.p. 50° (14).]

$\bar{C}$  with  $C_6H_5CH_2MgCl$  gives (54% yield (17)) benzyl-cyclopentyl-carbinol, b.p. 166–169° at 20 mm., m.p. 30° (3,5-dinitrobenzoate, m.p. 100.5–101.5° (17)). —  $\bar{C}$  with excess MeMgI gives (50% yield (13)) mixt. of both *cis* and *trans* 2-methylcyclohexanols (1:6420). —  $\bar{C}$  with cyclohexyl MgCl (cf. 3:8040) yields (18) cyclohexyl-cyclopentyl-carbinol, m.p.

34° (*p*-nitrobenzoate, m.p. 49–50°, 3,5-dinitrobenzoate, m.p. 102°, acid phthalate, m.p. 92–93°, *N*-phenylcarbamate, m.p. 122° (18)).]

[ $\bar{C}$  with conc. aq.  $NH_4OH$  shaken for 24 hrs. (19) or  $\bar{C}$  with  $NH_3$  in alc. htd. in s.t. for 1 hr. (6) gives (yields: 71% (19), 61% (6)) *cis*-2-aminocyclohexanol [Beil. X111-348], m.p. 65° (19) (6), b.p. 110° at 24 mm. (19). —  $\bar{C}$  with diethylamine (2 moles) htd. in s.t. at 150° for several hrs. (20) (or similarly with  $BuOH$  as solvent (21)) yields 2-(diethylamino)-cyclohexanol, b.p. 225° at 740 mm. (21), 224° at 730 mm. (20),  $D_{25}^{25} = 0.9280$  (21),  $n_D^{24} = 1.4659$  (21) (hydrochloride, m.p. 170.5–171.5° (21)). —  $\bar{C}$  with 5 pts. piperazine hydrate htd. 3 hrs. at 140° gives (22) both *N,N'*-bis-(2-hydroxycyclohexyl)piperazine, m.p. 205–206° (22), and *N*-(2-hydroxycyclohexyl)piperazine, m.p. 67–68° (22) (the latter separable by treatment of mixt. with  $CS_2$  pptg. its dithiocarbamate).]

[ $\bar{C}$  also reacts as a secondary alcohol: o.g.,  $\bar{C}$  with  $PCl_5$  yields (14) 1,2-dichlorocyclohexane [Beil. V-22, V<sub>1</sub>-(8)], b.p. 187–189°,  $\bar{C}$  with  $PBr_3$  yields (14) 1-bromo-2-chlorocyclohexane, b.p. 94° at 17 mm.,  $D_{20}^{20} = 1.514$ ,  $n_D^{20} = 1.5481$  (14).]

$\bar{C}$  on oxidn. with  $K_2Cr_2O_7/H_2SO_4/AcOH$  gives (57% yield (9)) 2-chlorocyclohexanone (3:0120).

(Note: the following derivatives are listed as *cis* on the assumption of inversion during formation.)

— *cis*(?) 2-Chlorocyclohexanyl acetate: oil with odor like  $EtOAc$ , b.p. 95–96° at 11 mm. (23), 99–101° at 13 mm. (24),  $D_{15}^{25} = 1.1182$  (23),  $n_D^{25} = 1.46195$  (23). [From  $\bar{C}$  with  $AcCl$  at 10–20° (23) or in  $C_6H_6$  (espec. in pres. of  $K_2CO_3$  or  $BaCO_3$ ) (70% yield (24)), or from cyclohexene (1:8070) with  $Ac_2O$  or with  $Ac_2O + SO_2Cl_2$  in  $CHCl_3$  (11).] [This ester with  $MeOH$  + dry  $HCl$  gas yields  $\bar{C}$  (11). Cf. (25).]

— *cis*(?) 2-Chlorocyclohexanyl benzoate: lfts. from dil. alc., m.p. 120–121° (24). [From  $\bar{C}$  with  $BzCl$  htd. 10 hrs. (70% yield) (24).]

— *cis*(?) 2-Chlorocyclohexanyl *p*-nitrobenzoate: cryst. from dil. alc., m.p. 240° dec. (24). [From  $\bar{C}$  with *p*-nitrobenzoyl chloride in dry ether or  $C_6H_6 + Na_2CO_3$  refluxed 5 hrs. (70% yield) (24).]

— *cis*(?) 2-Chlorocyclohexanyl *N*-phenylcarbamate: m.p. 97–98° (2), 94–96° (17). [From  $\bar{C}$  with phenyl isocyanate in lt. pct. (17).]

— *cis*(?) 2-Chlorocyclohexanyl *N*-( $\alpha$ -naphthyl)carbamate: m.p. 165° (3). [From  $\bar{C}$  with  $\alpha$ -naphthyl isocyanate at 100° for 4 hrs. (3).]

3:0175 (1) Godehot, Mousseron, Granger, *Compt. rend.* 299, 748–749 (1933). (2) Godehot, *Compt. rend.*, 1933, 1195. (3) Godehot, *Compt. rend.*, 1933, 1196. (4) Johnstone, *Or* (1932); 5, 31– (1926). (6) Soc. 73, 948 1938, 11 952.

Dirsch, *Ber.* 58, 574 (1925).

(11) Friese, Dj'iang, *Ber.* 71, 667–670 (1938). (12) Osterberg, *Org. Syntheses*, Coll. Vol. 1 (2nd ed.), 185–186 (1941); Coll.

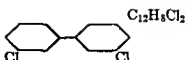
Bedos, *Bull. soc. chim.* (4) 37, 327–328 (1937). (15) Consolidated, 1, 205, 3835.

(16) Kötze, Busch, *J. prakt. Chem.* (2) 119, 36 (1928). (17) Cook, Hewitt, Lawrence, *J. Chem. Soc.* 1936, 74–75. (18) Vavon, Mitchovitch, *Compt. rend.* 186, 703–705 (1928). (19) Wilson, Read, *J. Chem. Soc.* 1935, 1272. (20) Osterberg, Kendall, *J. Am. Chem. Soc.* 43, 1370–1371 (1921).

(21) Heckel, Adams, *J. Am. Chem. Soc.* 49, 1305–1306 (1927). (22) Mousseron, *Bull. soc. chim.* (4) 51, 790–793 (1932). (23) Bedos, *Compt. rend.* 183, 562–565 (1926); *Cent.* 1926, 11 2795.

(24) Kötze, Merkel, *J. prakt. Chem.* (2) 113, 64–65 (1926). (25) Winstein, Buckles, *J. Am. Chem. Soc.* 65, 616 (1943). (26) Newman, Vander Werf, *J. Am. Chem. Soc.* 67, 235 (1945).

## 3:0180 3,3'-DICHLOROBIPHENYL

 $C_{12}H_8Cl_2$ 

Beil. V - 570

V<sub>1</sub>-(272)V<sub>2</sub>-(484)

M.P. 20° (1) (6) B.P. 322-324° (2)

23° (2) (3) 320-326° (4)

320-330° (1)

298° (6)

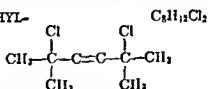
White ndls. from dil. alc.; eas. sol. alc., ether,  $C_6H_6$ .

[For prepn. of  $\bar{C}$  from *m*-chloriodobenzene [Beil. V-220] by htg. with Cu powd. under various conditions (yield: 95% (5), 67% (2), 61% (1)) see indic. refs.; from 3,3'-dinitrobiphenyl with  $SOCl_2$  in a.t. at 200-210° for 10 hrs. see (4), from 3,3'-dichloro-4,4'-diaminobiphenyl (3,3'-diaminobenzidine) [Beil. XIII-234, XIII<sub>1</sub>-(67)] via tetrazotization and htg. with alc. see (6); from 3,3'-dichloro-2,4'-diaminobiphenyl via tetrazotization and treatment with  $H_3PO_2$  see (3).]

$\bar{C}$  on tetranitration, e.g., with mixt. of 5 pts. abs.  $HNO_3$  + 20 pts. conc.  $H_2SO_4$  for 2 hrs. at 100° (5), yields (5) (7) 3,3'-dichloro-4,6,4',6'-tetranitrobiphenyl [Beil. V<sub>1</sub>-(274)], m.p. 191° (5), 189° (7), 184° (5); note that this prod. appears to exist in two forms: when the lower-melting form is dislvd. in boilg. AcOH and pptd. with boilg. nq, or if it is allowed to solidify after fusion, the prod. has m.p. 191°; if the above AcOH soln. is slowly cooled, however, the prod. melts at 184° (5). [This tetranitro- $\bar{C}$  htd. with  $NaOMe$  in MeOH yields 3,3'-dimethoxy-4,6,4',6'-tetranitrobiphenyl, m.p. 244° (5).] — [Note also that under some conditions (7) some 3,3'-dichloro-6,6'-dinitrobiphenyl [Beil. V-585, V<sub>1</sub>-(274)], m.p. 170° (8) (7), may form during nitration of  $\bar{C}$ .]

$\bar{C}$  on oxidn. with  $CrO_3$  +  $V_2O_5$  yields (3) *m*-chlorobenzoic acid (3:4392).

3:0180 (1) Weisseberger, Sängewald, *Z. physik. Chem.* B-20, 155 (1933). (2) Ullmann, *Ann.* 332, 54 (1904). (3) Bellavita, *Gazz. chim. ital.* 65, 641 (1935). (4) Mascarelli, Gatti, *Gazz. chim. ital.* 59, 508-509 (1929). (5) van Alphen, *Rec. trav. chim.* 51, 362-363 (1932). (6) Cain, *J. Chem. Soc.* 85, 7 (1904). (7) Borsche, Scholten, *Ber.* 50, 610 (1917). (8) Ullmann, *Organ. Ber.* 34, 3504 (1901).

— 2,6-DICHLORO-2,6-DIMETHYL-  
HEXYNE-3 $C_8H_{12}Cl_2$ 

Beil. I —

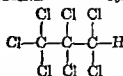
I<sub>1</sub>-(121)I<sub>2</sub>—

M.P. 29°

B.P. 62-63° at 15 mm.

See 3:9504. Division C: Liquids with b.p. reported only at reduced pressure.

3:0200 1,1,1,2,2,3,3-HEPTACHLOROPROPANE  $C_3HCl_7$  Beil. I - 108  
(*unsym.*-Heptachloropropane)  $I_1$ -(35)  
 $I_2$ -(73)



M.P. 29.40° (1) (4) B.P. 247-248° sl. dec. (3) (4)  $D_4^{24} = 1.8048$  (4)  
29-30° (2) (3) 163-166° at 90 mm. (5)  
30° (10) 150-151° at 50 mm. (3)  
147° at 43 mm. (4)  
137-140° at 32 mm. (2)  
122° at 25 mm. (10)  
110-113° at 10 mm. (2)

Hard cryst. with camphoraceous odor (3). [For crystallographic constants see (9).]

[For prepn. from tetrachloroethylene (3:5460) (or pentachloroethane (3:5880) (2) (3)) +  $\text{CHCl}_3$  (3:5050) by condensation in presence of  $\text{AlCl}_3$  (88-93% yield (2), 85% yield (1) (10)) see (1) (2) (5) (7); from pentachloroacetone (3:6205) by hgt. with  $\text{PCl}_5$  in s.t. at 180° for 6-8 hrs. see (3); from dichloroacetyl chloride (3:5290) with  $\text{AlCl}_3$  on warming ( $\text{CO} + \text{CHCl}_3 + \text{HCl}$  are also formed) see (11).]

$\bar{C}$  has large mol. freezing-point lowering, viz., 120° (6). [For use in detn. of mol. wt. of org. compds. by f.p. lowering see (6).]

$\bar{C}$  on hgt. especially in presence of catalysts such as  $\text{ZnCl}_2$  yields  $\text{HCl} + \text{hexachloropropene}$  (3:6370); with  $\text{CuCl}$  a second reaction also occurs yielding  $\text{HCl}$  and tetrachloroethylene (3:5460). [For extensive study of these see (7) (8).]

$\bar{C}$  in alc. on titration with alk. gives (4) (3) an apparent  $N_{\text{cut}}$  Eq. of 285.5 because of loss of 1  $\text{HCl}$  and formation of hexachloropropene (3:6370).

3:0200 (1) Frins, *Rec. trav. chim.* 54, 249-252 (1935). (2) Farlow, *Org. Syntheses* 17, 58-59 (1937). (3) Fritsch, *Ann.* 297, 314 (1897). (4) Frins, *J. prakt. Chem.* 89, 415-416 (1914). (5) Henne, Ladd, *J. Am. Chem. Soc.* 60, 2491-2495 (1938). (6) Böeseken, Benedictus, *Rec. trav. chim.* 37, 121-129 (1918). (7) Böeseken, van der Scheer, de Voogt, *Rec. trav. chim.* 34, 78-85 (1915). (8) Böeseken, *Rec. trav. chim.* 34, 585-587 (1915). (9) Böeseken, *Rec. trav. chim.* 34, 585-587 (1915). (10) Böeseken, *Rec. trav. chim.* 34, 585-587 (1915). (11) Böeseken, *Rec. trav. chim.* 34, 585-587 (1915).

3:0220 *p*-CHLOROBENZYL CHLORIDE  $C_7H_6Cl_2$  Beil. V - 297  
 $\text{Cl}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$   $V_1$ -(152)  
 $V_2$ -(231)

M.P. 30° (1) B.P. 217-218° at 772 mm. (8)  
29° (2) (3) (4) 214° at 758 mm. (3)  
(5) (6) (7) (35) 214° (9) (10)  
28.2-28.4° (12) 213-214° (11)  
26° (8) 114-117° at 30 mm. (35)  
114° at 25 mm. (12)  
113-115° at 24 mm. (13)  
106.5-107.5° at 23 mm. (14)  
117° at 20 mm. (3)  
94-96° at 14 mm. (8)

Cryst. from alc.,  $\text{AcOH}$  or lgr. — Eas. sol. warm but less so cold alc., very eas. sol. ether,  $\text{AcOH}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CS}_2$ . — Sublimes at ord. temp. — At b.p. under ord. press. tends to decompose (7). —  $\bar{C}$  has agreeable arom. odor, but strongly attacks mucous membrane (2).

[For prepn. of  $\bar{C}$  from benzyl chloride (3:8535) with  $Cl_2$  in pres. of  $I_2$  (11) (8) (15) or  $SbCl_5$  (16) see indic. refs.; from *p*-chlorotoluene (3:8287) with  $SO_2Cl_2 + Bz_2O_2$  in dark (70% yield) (35), with  $Cl_2$  in light (2) (17) (11) (5) (4) (18) (19) or with  $PhCl_4 \cdot 2NH_4Cl$  (9) see indic. refs.; from toluene with  $Cl_2$  see (20); for prepn. of  $\bar{C}$  from chlorobenzene (3:7903) with  $CH_2O + HCl$  (36), with bis-(chloromethyl) ether (3:5245) or chloromethyl methyl ether (3:7085) (formed by use of formaldehyde or paraformaldehyde + chlorosulfonic acid + conc.  $H_2SO_4$  or hexamethylenetetramine + conc.  $HCl$  (3)) as directed (50% yield (3)) (1) see indic. refs.]

$\bar{C}$  with phenol in toluene yields (21) 2-(*p*-chlorobenzyl)phenol, m.p. 60–61°, and *p*-chlorobenzyl phenyl ether, m.p. 85.5–86.5°;  $\bar{C}$  with 2,4-dichlorophenol in toluene yields (21) 2-(*p*-chlorobenzyl)-4,6-dichlorophenol, m.p. 69.5–70.5°, and *p*-chlorobenzyl 2,4-dichlorophenyl ether, m.p. 64.5–65.5°.]

$\bar{C}$  with phenol +  $AlCl_3$  yields (21) 4-(*p*-chlorobenzyl)phenol, m.p. 87–87.5° (benzoate, m.p. 115–116°);  $\bar{C}$  with 2,6-dichlorophenol +  $AlCl_3$  yields (21) 4-(*p*-chlorobenzyl)-2,6-dichlorophenol, m.p. 61.5–62.5° (benzoate, m.p. 116–117°).]

[For condens. of  $\bar{C}$  with *p*-chlorophenol (3:0475) and use of prod. as anti-moth prepn. see (22); for condens. of  $\bar{C}$  with *o*-cresol (1:1400) or its Na salt or with 3,5-dimethylphenol (*sym*-*m*-xylenol) (1:1455) and use of products as bactericides see (23); for condens. of  $\bar{C}$  with sulfonated phenol and use as tanning agent see (24); for condens. of  $\bar{C}$  with resorcinol (1:1530) +  $AlCl_3$  in nitrobenzene yielding 55% 4-(*p*-chlorobenzyl)resorcinol see (25).]

$\bar{C}$  with Mg in dry ether yields (10) *p*- $Cl.C_6H_4.CH_2$  MgCl which with phenyl isocyanate as directed (10) gives *p*-chlorophenylacetanilide [Beil. XII-275], lfts. from alc., m.p. 168° cor. (26), 165–166° u.c. (10), 164.5° (27)

$\bar{C}$  on boilg. with aq. (2) (3) hydrolyzes to *p*-chlorobenzyl alc. [Beil. VI-444], m.p. 70–71° (3) (for rate see (7));  $\bar{C}$  on boilg. with  $Ph(NO_2)_2$  for 2 days (28) or on boilg. in 60% alc. with hexamethylenetetramine (29) yields *p*-chlorobenzaldehyde (3:0765), m.p. 46–47° (3).

$\bar{C}$  with alc. KOH yields (30) *p*-chlorobenzyl ethyl ether [Beil. VI-444, VI<sub>1</sub>-(222)], oil, b.p. 225° (for study of rate of reactn. see (31));  $\bar{C}$  with KOAc in abs. alc. yields (28) *p*-chlorobenzyl acetate [Beil. VI-445], b.p. 240° (28);  $\bar{C}$  with boilg. alc. KCN yields (11) (28) (20) *p*-chlorobenzyl cyanide [Beil. LX-448], m.p. 30° (20), h.p. 265–267° (20), which on hydrolysis yields *p*-chlorophenylacetic acid (3:3135), m.p. 105° (20).

$\bar{C}$  with KI in alc. gives alm. quant. yield (17) *p*-chlorobenzyl iodide, m.p. 64° (17) (for study of rate of reactn. of  $\bar{C}$  with NaI (34) or KI (14) (6) in acetone see indic. refs.);  $\bar{C}$  with  $Na_2SO_3$  yields (18) (13) sodium *p*-chlorotoluene-*o*-sulfonate (corresp. sulfonamide, m.p. 157° (18), corresp. sulfonanilide, m.p. 235° (18)).

$\bar{C}$  with thiourea (1 mole) in alc. refluxed 30 min. gives (37) *S*-(*p*-chlorobenzyl)isothiurea hydrochloride (*p*-chlorobenzyl isothiuronium chloride), cryst. from 1:1 conc.  $HCl + aq.$ , m.p. 197°; this prod. is useful in identification of organic acids (37) ]

$\bar{C}$  on oxidn. with  $CrO_3$  (11) (3) or with  $KMnO_4$  (1) (12) yields *p*-chlorobenzoic acid (3:4940), m.p. 236°.

3:0220

on, Field, Ber. 11, 904–905

(4) Jones, J. Chem. Soc.

147 (1933). (6) Bennett.

. 41, 307–308 (1921). (8)

. 41, 307–308 (1921). (8)

W. Engel, Z. physik. Chem. B-15, 96 (1931–2). (9) Seyenetz, Trawitz, Compl. rend. 136,

241 (1903). (10)

(11) Beilstein, 3

J. Am. Chem. Soc.

(14) Conant, Kirt

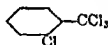
419–421 (1921).

15, 388–392 (189

(20) von Walther, 4639-4643 (1933).  
 (23) Klarmann, Gates (to Lehn and Fink, Inc.), U.S. 1,926,873, 1,926,874, Sept. 12, 1933; *Cent.* 1934, I 83.  
 (24) I.G., Brit. 320,056, Oct. 31, 1929; *Cent.* 1930, I 590; Brit. 321,190, Nov. 28, 1929; *Cent.* 1930, I 1259. (25) Klarmann, von Wövern, *J. Am. Chem. Soc.* 51, 608 (1929). (26) Jenkins, Richardson, *J. prakt. Chem.* (2) 62, 562 (1900). (28) (29) Mayer, *English, Ann.* 417, 78-79 (1933). (31) 331-335 (1921). (32) Kindler, *Ann.* 452, 377-378 (1903). (34) h, Brown, *J. Am. Chem. Soc.* 61, Oct. 8, 1933; *Cent.* 1931, I 360 61, 3251-3252 (1939).

—  $\alpha$ -CHLOROBENZOTRICHLORIDE $C_6H_4Cl_4$ 

Beil. V - 302

V<sub>1</sub>-(153)V<sub>2</sub>-(234)

M.P. 30°

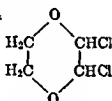
B.P. 260°

See 3:6880. Division B: Liquids, Section 1,  $D_4^{20} > 1.15$ .

## — 2,3-DICHLORODIOXANE-1,4

 $C_4H_6O_2Cl_2$ 

Beil. S.N. 2668



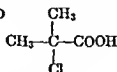
M.P. 30°

B.P. 100-101° at 24-25 mm.

See 3:9105. Division C: Liquids with b.p. only at reduced pressure.

3:0235  $\alpha$ -CHLORO-ISOBUTYRIC ACID $C_4H_7O_2Cl$ 

Beil. II-294

II<sub>1</sub>—II<sub>2</sub>—

M.P. 31° (1) (2) B.P. 118° at 50 mm. (1)

28-30° (3) 116-118° at 50 mm. (4)

80-82° at 12 mm. (2)

Eas. sol. aq.

[For prepn. of  $\bar{C}$  from isobutyric acid (1:1030) with  $Cl_2$  in light (5) (10) or with cat. as specified (6) (7), or with  $SO_2Cl_2$  + dibenzoyl peroxide in  $CCl_4$  (15%  $\bar{C}$  + 85%  $\beta$ -chloro isomer) (3:9132) (3), see indic. refs.; from  $\beta,\beta,\beta$ -trichloro-*tert*-butyl alc. ("Chloreton") (3:2662) with aq. alk. (small yield together with other prods.) see (1) (2); from 2-chloro-2-methylpropanol-1 ( $\beta$ -chloro-isobutyl alc.) (3:7305) by oxidn. with conc.  $HNO_3$  see (8); from  $\alpha$ -chloro-isobutyryl chloride (3:5385) by hydrolysis with aq. see (9).]

$\bar{C}$  with aq. alk. yields (5)  $\alpha$ -hydroxy-isobutyric acid (1:0431) together with other products. —  $\bar{C}$  with aq.  $Ca(OCl)_2$  yields (4) chloroform (3:5050) +  $AcOH$  (1:1010) +  $CO_2$ .

$\bar{C}$  with  $SOCl_2$  (11) yields  $\alpha$ -chloro-isobutyryl chloride (3:5385), b.p. 117-118°.

— Methyl  $\alpha$ -chloro-isobutyrate: b.p. 129° (see 3:7918).

— Ethyl  $\alpha$ -chloro-isobutyrate: b.p. 148° (see 3:8147).

—  $\alpha$ -Chloro-isobutyramide: unreported.

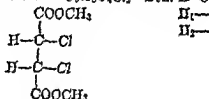
②  $\alpha$ -Chloro-isobutyryl-anilide: m.p. 71-71.5° (3), 68° (12), 67-68° (13). [From  $\alpha$ -chloro-isobutyryl chloride with aniline (3).] [Note that  $\beta$ -chloro-isobutyryl-anilide has m.p. 109.0-109.5° (3).]

③  $\alpha$ -Chloro-isobutyro- $p$ -toluidide: unreported.

3:0235 (1) Ostropjatow, *J. Russ. Phys.-Chem. Soc.* 28, 50 (1896), *Ber.* 29, Referate, 908-909 (1896). (2) Jacob, *Bull. soc. chim.* (5) 7, 581-586 (1940); *C.A.* 36, 3507 (1942). (3) Kharasch, *Repts. J. Am. Chem. Soc.* 62, 605-606 (1940); *J. Org. Chem.* 5, 1216 (1940).

11  
Dow  
order,  
(8)  
kind,

3:0240 DIMETHYL *meso*- $\alpha,\alpha'$ -DICHLOROSUCCINATE  $C_6H_8O_4Cl_2$  Beil. II-619



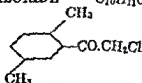
M.P. 31.5-32° (1)

[For prepn. of  $\bar{C}$  from *meso*- $\alpha,\alpha'$ -dichlorosuccinic acid (3:4930) in MeOH with HCl gas see (1).]

[For studies on dipole moment see (2).]

3:0240 (1) Kirchhoff, *Ann.* 286, 215 (1894). (2) Hassel, *Nasenhagen, Tids. Kemi Berpøtten* 10, 126-127 (1930); *Cent.* 1931, I 893, *C.A.* 25, 1493 (1931).

3:0245 2,5-DIMETHYLPHENACYL CHLORIDE  $C_{10}H_{11}OCl$  Beil. VII-324  
( $\omega$ -Chloro-2,5-dimethyl  
acetophenone)  $\text{VII}_1-$



M.P. 32°

[For prepa. from *p*-xylene, chloroacetyl chloride (3:5235) +  $\text{AlCl}_3$ , see (1) (2).]

$\bar{C}$  on oxidn. with alk.  $\text{KMnO}_4$  gives (2) trimellitic ac. (1:0551), m.p. 228°.

3:0245 (1) Kuncell, *Ber.* 30, 579 (1897). (2) Collet, *Bull. soc. chim.* (3) 17, 509 (1897).



[ $\bar{C}$  with liq.  $NH_3$  as directed (39) gives 72%  $\alpha$ -naphthylmethylamino (*N*-benzoyl deriv., lfts. from alc., m.p. 154° (1)) + 20% bis-( $\alpha$ -naphthylmethyl)amine (*N*-benzoyl deriv., pr. from alc., m.p. 134° (1)). —  $\bar{C}$  with alc.  $NH_3$  as directed (39) gives 11% of the above prim. amine + 38% of the above sec. amine + 47% tris-( $\alpha$ -naphthylmethyl)amine, cryst. from alc., m.p. 178° (39). — Note the use of the above bis-( $\alpha$ -naphthylmethyl)amine as useful reagent for quant. pptn. of  $HNO_3$  (6). — For reactn. of  $\bar{C}$  with  $(CH_3)_2NH$  see (1). —  $\bar{C}$  with aniline at 100° gives (77% yield (4)) *N*-( $\alpha$ -naphthylmethyl)aniline, m.p. 67° (4) (corresp. nitroso cpd., m.p. 57° (4)).]

[ $\bar{C}$  with thiourea in alc. as directed (40) yields *S*-( $\alpha$ -naphthylmethyl)isothioureia hydrochloride, m.p. 238° (40). —  $\bar{C}$  with *p*-toluenesulfonamide + alc. KOH refluxed 12 hrs. gives (57% yield (6)) *N,N*-bis-( $\alpha$ -naphthylmethyl)*p*-toluenesulfonamide, cryst. from boilg. alc., m.p. 134° (6).]

[ $\bar{C}$  with various polynitrophenols gives addn. prods.: e.g., that from picric acid has m.p. 80–82° (41), 84° (4); that from 2,4,6-trinitro-*m*-cresol has m.p. 81.5–82° (41); that from 2,4,6-trinitroresorcinol (styphnic acid) has m.p. 112.5–113° (41).]

- ① *N*-( $\alpha$ -Naphthylmethyl)phthalimide ( $\alpha$ -phthalimido- $\alpha$ -methylnaphthalene): white ndls, from hot alc., m.p. 174–175° (6). [From  $\bar{C}$  + Na phthalimide refluxed 6 hrs. in alc. in 82% yield (6).] — [Hydrolysis of this prod. with 4 pts. conc. HCl in a.t. 2 hrs. at 100° gives (86% yield (6))  $\alpha$ -naphthylmethylamine (see above).]

3:0250 (1) von Braun, Moldaenke, *Ber.* 56, 2167–2172 (1923). (2) Manske, Ledingham, *Can. J. Research* 17-B, 14–20 (1939); *Cent.* 1939, I 4037; *C.A.* 33, 5387 (1939). (3) Darzens, Levy, *Compt. rend.* 202, 73–75 (1936). (4) Anderson, Short, *J. Chem. Soc.* 1933, 485. (5) de Pommerau, *Compt. rend.* 175, 105–100 (1922). (6) Rupe, Brentano, *Helv. Chim. Acta* 19, 581–586 (1936). (7) Reddell, Lange (to I.G.), *Ger.* 508,890, Oct. 2, 1930; *Brit.* 337,280, Nov. 20, 1930; *Cent.* 1931, I 1530. (8) von Braun, Nelles, *Ber.* 66, 1470 (1933). (9) Davies, Oxford, *J. Chem. Soc.* 1931, 220–221. (10) Vavon, Bolle, Callin, *Bull. soc. chim.* (5) 6, 1032–1033 (1939).

(11) Coles, Dodds, *J. Am. Chem. Soc.* 60, 853–854 (1938). (12) Scherler, *Ber.* 24, 3929–3030 (1891). (13) Lock, Walter, *Ber.* 75, 1158–1101 (1912). (14) Wislicenus, Wren, *Ber.* 38, 506–507 (1905).

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(31) Briggs, Wilson, *J. Chem. Soc.* 1941, 577; *Cent.* 1941, I 2396. (32) Briggs, Wilson, *J. Chem. Soc.* 1941, 577–578; *Cent.* 1941, I 2396. (33) *C.A.* 27, 81 (1933). (34) Deutsche Hydrier 4397. (35) I.G., *French* 811,273, April 10, 1931; *Cent.* 1931, I 2396. (36) I.G., *Brit.* 462,290, April 1, 1937; *Cent.* 1937, I 2456. (37) Kränzlein, Voss, Brunner, *Ger.* 526,391, June 5, 1931; *Cent.* 1931, II 1203. (38) von Braun, *Ber.* 70, 979–980, 983–984 (1937). (39) Sprague, Johnson, *J. Am. Chem. Soc.* 59, 1839 (1937).

(40) Dermer, *Proc. Oklahoma Acad. Sci.* 22, 160–162 (1941); *C.A.* 37, 4376 (1943). (41) Izmail'skii, Kozin, *Compt. rend. acad. sci. U.R.S.S.* 28, 621–624 (1940); *C.A.* 35, 2882 (1941).

(42) Izmail'skii, *Compt. rend.* Grummitt, Buck, *Org. Syntheses* 1, 58, 28 (1936). (43) Shmuk, 39, 4069 (1945).

3:0255 *m*-CHLOROPHENOL $C_6H_5OCl$ 
 Beil. VI - 185  
 VI<sub>1</sub>-(99)  
 VI<sub>2</sub>-(172)

M.P. 32.8° (1)	B.P. 215.5-217.1° (7)	$D_4^{20} = 1.237$ (9)	$n_D^{20} = 1.5565$ (1)
32° (2)	216° (17)	$D_4^{25} = 1.268$ (9)	
31-32° (3)	213-216° (8)		
31° (4)	214° (6) cor. (16)		
28.5° (5)	211-212° u.c. (5)		
28° (6)	98° at 12 mm. (2)		

$\bar{C}$  has odor like phenol (for study of strength of odor in aq. soln. see (10)). —  $\bar{C}$  in pres. of aq. has unusual tendency to form supersatd. solns (11) (for temp./compn. data on soly. of  $\bar{C}$  in aq. or in  $C_6H_6$  see (11)). —  $\bar{C}$  cas. discolors in air.

[For prepn. of  $\bar{C}$  from *m*-chloroaniline [Beil. XII-602, XII<sub>1</sub>-(300)] via diazotization and subsequent reaction with aq. yields: alm. quant. (12) (13), 67% (1), 64% (8), 55% (4), 50% (14) (15) (5) (16) see indic. refs. (note that the process is sensitive to conditions and refs. indic. give valuable information on its control); for formn. of  $\bar{C}$  from *m*-dichlorobenzene (3:5960) with NaOMe in MeOH in s.t. at 180° for 30 hrs. see (17).]

$\bar{C}$  like its isomers is sol. in conc.  $Na_2CO_3$  soln. at room temp. and is reprecip. by  $CO_2$  (18). [For studies of value of ionization const. of  $\bar{C}$  in aq. or dil. MeOH or dil. EtOH see (19) (20) (6) (21) (22).]

$\bar{C}$  on fusion with KOH yields (23) resorcinol (1:1530). — [For condens. of  $\bar{C}$  with phthalic anhydride to yield 3,6-dichlorofluorane ("fluorescein chloride") [Beil. XIX-147] (impt. intermed. in prepn. of rhodamine dyes) see (12) (58).]

$\bar{C}$  conv. to dry Na salt and treated with  $CO_2$  under press. yields after acidifn. (14) 6-carboxy-3-chlorophenol (4-chloro-2-hydroxy benzoic acid) (4-chlorosalicylic acid) (3.4008), ndls. from aq., m.p. 207° (14).]

$\bar{C}$  in the Reimer-Tiemann reactn. with alk. (or better  $Ca(OH)_2 + Na_2CO_3$  (24)) and chloroform (24) or bromoform (25) yields both 6-aldehydo-3-chlorophenol (4-chlorosalicylaldehyde) (3.0960) and 4-aldehydo-3-chlorophenol (3.4250) in *o/p* ratio of 0.71 with  $CHCl_3$  (26) (25) and 0.84 with  $CHBr_3$  (25). — [The 4-aldehydo-3-chlorophenol has also been obt'd. (50% yield) from  $\bar{C}$  in  $C_6H_6$  with  $HCl + HCN + AlCl_3$  (29).]

$\bar{C}$  in aq.  $Na_2CO_3$  soln. couples with 1 equiv. of benzenediazonium chloride yielding (27) (18) 3-chloro-4-phenylazophenol, or -yel. ndls. from 25% AcOH, m.p. 95° (27), or, on expos. to  $HCl$ , or -red, m.p. 114° (27) (18);  $\bar{C}$  in aq. NaOH with 2 equivs. of benzenediazonium chloride yields (27) 3-chloro-2,4-bis(phenylazo)phenol, dark red-brn., m.p. 181°; no bis-azo epds. appear to be formed (27). — For study of coupling of  $\bar{C}$  with *p*-nitrobenzenediazonium bisulfate see (28).

$\bar{C}$  is not reduced by  $HI$  in AcOH (30); for study of replacement of  $Cl$  by  $H$  with  $H_2 + Ni$  cat. at room temp. see (31).]

$\bar{C}$  with *p*-aminophenol oxidized in alk. soln. with NaOCl yields (32) indo-chlorophenol;  $\bar{C}$  with *p*-aminodimethylaniline on oxidn. with NaOCl as directed (5) yields 3-chloro-*N,N*-dimethylindooaniline.]

[For condensation of  $\bar{C}$  with formaldehyde (33) or with benzaldehyde-*o*-sulfonic acid (34) and use of product as mothproofing agents see indic. refs.; for reactn. of  $\bar{C}$  with unsatd. halides in pres. of alk. yielding *m*-chlorophenyl allyl ethers which by rearn. yield corresp. substituted phenols used as bactericides see (35) (36).]

[For condens. of  $\bar{C}$  with malic acid (1.0450) + conc.  $H_2SO_4$  giving small yield of 7-chlorocoumarin [Beil. XVII-331] see (37); with ethyl acetoacetate (1:1710) +  $H_2SO_4$

giving small yield of 7-chloro-4-methylenumarin [Beil. XVII-336] see (37); with ethyl methylacetacetate (1:1712) +  $P_2O_5$  yielding 7-chloro-2,3-dimethylchromone [Beil. XVII-1-177] see (38).]

$\bar{C}$  with 3 moles  $Br_2$  (in aq.  $KBr$ ) gives 100% yield (39) 2,4,6-tribromo-3-chlorophenol, ndls. from dil. alc., m.p. 105–106° cor. (39) (methyl ether, m.p. 06° (39));  $\bar{C}$  in 10% aq.  $KOH$  with 4 moles  $I_2$  (in aq.  $KI$ ) gives 2,4,6-triiodo-3-chlorophenol; ndls. from boilg.  $AcOH$ , m.p. 139–140° (39).

[ $\bar{C}$  in dil.  $NaOH$  mixed with aq.  $NaNO_2$  and acidified as directed (40) gives (40% yield (40)) (43) 3-chloro-4-nitrosophenol, m.p. 133° (40), 129.6° (41); on soln. in  $Na_2CO_3$  and subsequent acidification this cpd. yields (40) (43) the isomeric 3-chlorobenzoquinone-4-monoxime, m.p. 184° dec. (40), cf. (42).]

[ $\bar{C}$  on mononitration with  $H_2SO_4$  +  $NaNO_3$  as directed (44) or  $\bar{C}$  in  $AcOH$  with fuming  $HNO_3$  at 0° (45) gives (yield: 32% (45), 22% (44)) 3-chloro-6-nitrophenol [Beil. VI-238], volatile with steam, m.p. 41° (44), together with (60% yield (44)) 3-chloro-4-nitrophenol [Beil. VI-240], not volatile with steam, white ndls. from dil.  $HCl$  or aq., m.p. 121–122° (44). — Note that the two other position isomers although known have been obtd. indirectly: 3-chloro-2-nitrophenol, anhydrous form, yel. cryst., m.p. 45–47° (46) (47); monohydrate, colorless cryst. from pct. ether, m.p. 37.5–38° (46) (47) (44); 3-chloro-5-nitrophenol [Beil. VI-239] (48), m.p. 147°.]

[ $\bar{C}$  on dinitration as directed (44) (49) gives 3-chloro-4,6-dinitrophenol [Beil. VI-250, VI-1-28], colorless cryst. from aq. or lt. pct., m.p. 92–93° (44). — Note that two other position isomers are known but prepd. indirectly: 3-chloro-2,6-dinitrophenol, white cryst. from dil.  $HCl$ , m.p. 114.5° (44) (49); 3-chloro-2,4-dinitrophenol, cryst. from aq., m.p. 138–140° (44) (49).]

$\bar{C}$  on trinitration by soln. in  $1\frac{1}{2}$  pts. fuming  $H_2SO_4$  (27%  $SO_3$ ) and treated in cold for 1 hr. with 10 pts. 70%  $HNO_3$  (44) cf. (4) (50) yields 3-chloro-2,4,6-trinitrophenol [Beil. VI-292], cryst. from aq. nr dil.  $H_2SO_4$ , m.p. 114° (44), 116° (4), 119° (50). — [Note that if  $\bar{C}$  is sulfonated prior to trinitration the isomeric 3-chloro-2,5,6-trinitrophenol, m.p. 112.5–113.5° (44), is obtd. (44).]

[For studies on the sulfonation of  $\bar{C}$  see (44) (51) (52) (53).]

[ $\bar{C}$  in  $MeOH/KOH$  with  $MeI$  yields (29) *m*-chlorophenyl methyl ether (*m*-chloroanisole) (8:6105).] [ $\bar{C}$  in  $EtOH/KOH$  with  $EtI$  gives (18) 3-chlorophenyl ethyl ether (*m*-chlorophenetole) (3:6323), b.p. 204–205° at 717 mm.,  $D_4^{20} = 1.1712$  (18) (for rate of formn. from sodium salt of  $\bar{C}$  with  $EtI$  in alc. soln. see (55)).]

— *m*-Chlorophenyl acetate [Beil. VI-185]: nil, b.p. 116.6° at 21 mm. (18), 108° at 12 mm. (57), 84–86° at 2 mm. (57), m.p.  $-1.5^\circ$  to  $-0.5^\circ$  (18),  $D_4^{20} = 1.2200$  (18).

[From  $\bar{C}$  with  $Ac_2O$  +  $NaOAc$  (18) nr indirectly from *m*-chloroaniline via diazotiazation, etc. (57).] [For rate of reactn. of  $\bar{C}$  with  $AcBr$  see (58).]

① *m*-Chlorophenyl benzoate [Beil. IX-117]: pr. from dil. alc. or dil. acetone, m.p. 71–72° (18). [From  $\bar{C}$  in 10% aq.  $Na_2CO_3$  with  $BzCl$  (18); for study of rate of benzoylation of  $\bar{C}$  see (59).]

② *m*-Chlorophenyl *m*-nitrobenzoate: ndls. from alc. or dil. acetone, m.p. 94–95° (18). [From  $\bar{C}$  in alk. with *m*-nitrobenzyl chloride (18).]

③ *m*-Chlorophenyl *p*-nitrobenzoate: m.p. 90°.

④ *m*-Chlorophenyl 3,5-dinitrobenzoate: m.p. 156°.

— *m*-Chlorophenyl benzenesulfonate: unrecorded.

— *m*-Chlorophenyl *p*-toluenesulfonate: unrecorded.

— *m*-Chlorophenyl benzyl ether: m.p. 59°. [From  $\bar{C}$  + benzyl-phenyl-dimethyl-ammonium chloride (60).]

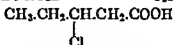
— *m*-Chlorophenyl *p*-nitrobenzyl ether: unrecorded.

- *m*-Chlorophenyl 2,4-dinitrophenyl ether: pale yel. ndls. from alc., m.p. 75° (61). [From  $\bar{C}$  in alk. with alc. 2,4-dinitrochlorobenzene (61).]
- ⑥ *m*-Chlorophenoxyacetic acid: cryst from aq., m.p. 108–110° u.c. (62), Neut. Equiv. 186.5. [From  $\bar{C}$  in aq. NaOH with chloroacetic acid (62).]
- *m*-Chlorophenyl *N*-phenylcarbamate: unrecorded.
- ⑦ *m*-Chlorophenyl *N*-(*p*-bromophenyl)carbamate: ndls. from  $C_6H_6$  + EtOAc, m.p. 121–123° cor. (64). [From  $\bar{C}$  + *p*-bromobenzazide in lgr. (64).]
- ⑧ *m*-Chlorophenyl *N*-(*p*-iodophenyl)carbamate: m.p. 138–139° (69). [From  $\bar{C}$  with *p*-iodobenzazide in hot lgr. (69).]
- ⑨ *m*-Chlorophenyl *N*-(*m*-nitrophenyl)carbamate: m.p. 115–116° u.c., 117–118° cor. (70). [From  $\bar{C}$  with *m*-nitrobenzazide or with *m*-nitrophenyl isocyanate in lgr. (70).]
- ⑩ *m*-Chlorophenyl *N*-(*p*-nitrophenyl)carbamate: pale yel. pr. from lgr., m.p. 144° cor. (65). [From  $\bar{C}$  + *p*-nitrobenzazide in lgr. (65).]
- ⑪ *m*-Chlorophenyl *N*-(3,5-dinitro-4-methylphenyl)carbamate: or.-yel. pr. from lgr., m.p. 170–172° u.c., 174–176° cor. (63). [From  $\bar{C}$  with 3,5-dinitro-4-methylbenzazide in lgr. (63).]
- ⑫ *m*-Chlorophenyl *N*-( $\alpha$ -naphthyl)carbamate: cryst. from lgr., m.p. 157–158° (66). [From  $\bar{C}$  +  $\alpha$ -naphthyl isocyanate in lgr. (66).]
- ⑬ *m*-Chlorophenyl *N*-( $\beta$ -naphthyl)carbamate: pr. from lgr., m.p. 114–115° u.c., 116–117° cor. (67). [From  $\bar{C}$  +  $\beta$ -naphthyl isocyanate (or azide) in lgr. (67).]
- *m*-Chlorophenyl *N,N*-diphenylcarbamate: unreported.

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- (31) Kelber, *Ber.* 54, 2255–2260 (1921). (32) Heller, *Ann.* 418, 270–271 (1918). (33) Weiler, Berres, Wenk, Stötter (to I.G.), *Ger.* 536,551, Oct. 24, 1931; *Cent.* 1932, I 3013. (34) I.G., Austrian 121,264, Aug. 25, 1931; *Cent.* 1931, II 3175. (35) Deichsel (to Winthrop Chem. Co.), U.S. 2,002,447, May 21, 1935; *Cent.* 1935, II 2581, C.A. 29, 4376 (1935). (36) Deichsel (to I.G.), Brit. 443,113, March 19, 1936; *Cent.* 1937, I 384, C.A. 30, 4573 (1936). (37) Clayton, *J. Chem. Soc.* 83, 2021–2022 (1905). (38) Simonis, Schuhmann, *Ber.* 50, 1146 (1917). (39) Kohn, Zandmann, *Monatsh.* 47, 362, 366 (1926). (40) Hodgson, Kershaw, *J. Chem. Soc.* 1929, 1553, 1555.
- (41) Hodgson, Moore, *J. Chem. Soc.* 123, 2502–2503 (1923). (42) Hodgson, Nicholson, *J. Chem. Soc.* 1910, 1268. (43) British Dyestuffs Corp., Ltd., & Hodgson, *Brit.* 200,734, Dec. 6, 1921; *Cent.* 1923, II 2094. (44) Hodgson, Moore, *J. Chem. Soc.* 127, 1599–1604 (1925). (45) Roberts, Rhye, *J. Chem. Soc.* 1937, 41. (46) Hodgson, Moore, *J. Chem. Soc.* 1926, 156, 158. (47) Hodgson, *J. Soc. Dyers Colourists* 43, 73 (1927). (48) Hodgson, Wignall, *J. Chem. Soc.* 1926, 2077. (49) Hodgson, Kershaw, *J. Chem. Soc.* 1930, 2169–2171. (50) Tijmstra, *Rec. trav. chim.* 21, 293 (1902).
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Van Natta, Clarkson, *J. Am. Chem. Soc.* 58, 2734 (1925). (54) Ghaswalla, Donne, *Chem. Soc.* 1926, 1254. (56) Réverdin, E, *J. Am. Chem. Soc.* 55, 4954-4955 (1933); Bassett, *J. Chem. Soc.* 1931, 2516-2518. (59) Bernoulli, St. Goar, *Helv. Chim. Acta* 9, 755 (1926). (60) Baw, *J. Indian Chem. Soc.* 3, 101-104 (1926). (61) Bost, Nicholson, *J. Am. Chem. Soc.* 57, 2368-2369 (1935). (62) Koelsch, *J. Am. Chem. Soc.* 53, 304-305 (1931). (63) Sah, *Rec. trav. chim.* 58, 587-588 (1939). (64) Sah, Cheng, *Rec. trav. chim.* 58, 592-593 (1939). (65) Sah, Cheng, *Rec. trav. chim.* 58, 596-599 (1939). (66) French, Wirtel, *J. Am. Chem. Soc.* 48, 1736-1739 (1926). (67) Sah, *Rec. trav. chim.* 58, 454-458 (1939). (68) British Dyestuffs Corp., Ltd., & Hodgson, Brit. 205,254, Nov. 8, 1923; *Cent.* 1924, I 711. (69) Sah, Young, *Rec. trav. chim.* 59, 357-363 (1940). (70) Sah, Woo, *Rec. trav. chim.* 58, 1014-1015 (1939).

3:0270 *d,l*- $\beta$ -CHLORO-*n*-VALERIC ACID  $C_5H_9O_2Cl$  Beil. S.N. 162



M.P. 33° (1) B.P. 112° at 10 mm. (1)  $D_4^{20} = 1.1484$  (1)  $n_D^{20} = 1.4462$  (1)

[For prepn. of  $\bar{C}$  from propylidene-acetic acid (penten-2-oic acid-1) [Beil. II-426, II<sub>1</sub>-(191), II<sub>2</sub>-(399)] with dry HCl gas at 20° for 2 days (100% yield) see (1).]

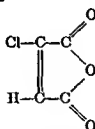
- Methyl  $\beta$ -chloro-*n*-valerate: unreported.
- Ethyl  $\beta$ -chloro-*n*-valerate: b.p. 189° see (3:8629).
- $\beta$ -Chloro-*n*-valeramide: unreported.
- $\beta$ -Chloro-*n*-valeraniide: unreported.
- $\beta$ -Chloro-*n*-valero-*p*-toluidide: unreported.

3:0270 (1) Schjanberg, *Ber.* 70, 2385-2391 (1937).

3:0280 CHLOROMALEIC ANHYDRIDE

$C_4HO_3Cl$

Beil. XVII-434  
XVII<sub>1</sub>—



M.P.	B.P.		
33° (1)	196.3° cor.	(2)	$D_{25}^{25} = 1.5421$ (2) $n_{H_2O}^{16.7} = 1.50594$ (1)
34.5° (2) (3)	194°		$D_4^{15} = 1.5427$ (1) $n_{H_2O}^{13.9} = 1.50933$ (1)
	150-151° at 210 mm.	(2)	
	95° at 25 mm.	(3A)	
	87° at 14 mm.	(1)	
	78° at 8 mm.	(1)	

$\bar{C}$  usually observed as a colorless oil. On cooling and scratching it solidifies to a cryst. mass fusing about 0° and suddenly changing to a hard cryst. form, m.p. 34.5°, with evoln. of ht. (2) (3).

[For prepn. from chlorofumaric ac. (3:4853) by distn. with  $P_2O_5$  see (1) (4), by distn. with  $POCl_3$  see (5) (such products are claimed by (1) to be impure); for prepn. by distn. with  $AcCl$  see (2); for still other methods see Beil. XVII-434.]

[For Diels-Alder addn. of  $\bar{C}$  to cyclopentadiene-1,3 (1:8030) giving 71% yield of prod. m.p. 161°, or to anthracene (1:7285), giving 56% yield of prod., m.p. 157°, see (7); note, however, that  $\bar{C}$  with isocugenol (1:1785) or with isosafrole (1:7610) not only adds but also loses HCl giving (8) derivs. of 3-methyl-3,4-dihydronaphthalene-1,2-dicarboxylic anhydride.]

$\bar{C}$  reacts with aq. evolving ht. and upon evapn. yields (3) (3A) (6) chloromaleic ac. (3:3432), cryst. from mixt. of  $CHCl_3$  +  $AcOH$  (6), which after drying at 100° have m.p. 114-115° (6).

3:0280 (1) von Auwers, Harres, *Ber.* 62, 1686-1687 (1929). (2) Perkin, *J. Chem. Soc.* 53, 703-705 (1888). (3) van der Riet, *Ann.* 286, 227 (1894) (3A) Zincke, Fuchs, *Ber.* 26, 508 (1893). (4) Walden, *Ber.* 30, 2885-2886 (1897). (5) Thomas-Mamert, *Bull. soc. chim.* (3) 13, 847 (1895). (6) Michael, Tissot, *J. prakt. Chem.* (2) 52, 331 (1895) (7) Synerholm, *J. Am. Chem. Soc.* 67, 1229-1230 (1945). (8) Synerholm, *J. Am. Chem. Soc.* 67, 345 (1945)

3:0290 TRICHLOROMETHYL TRICHLOROACETATE  $C_2O_2Cl_6$  Beil. III -17  
(Perchloromethyl acetate)  $Cl_3C.O.CO.CCl_3$  III<sub>1</sub>—  
III<sub>2</sub>—

M.P. 34° (1) B.P. 191-192° (1)  $D_4^{35} = 1.67331$  (1)  
73-74° at 10 mm. (1)

Sol. without decompn. in ether,  $CHCl_3$ ,  $C_6H_6$ , or pet. eth.

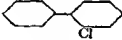
[For prepn. (71% yield (3)) by electrolysis of potassium trichloroacetate (3) or mixt. of Na and Zn trichloroacetates (2) (4) see (2) (3) (4); for formn. from methyl trichloroacetate on chlorination see (1).]

$\bar{C}$  with aq. decomposes to trichloroacetic acid (3:1150) + phosgene (3:5000) + HCl (2) (4).

$\bar{C}$  with aniline yields *N,N'*-diphenylurea + aniline trichloroacetate + aniline hydrochloride (2).

$\bar{C}$  with  $AlCl_3$  yields hexachloroethane (3.4835) +  $CO_2$  (5).

3:0290 (1) Anschütz, Emery, *Ann.* 273, 59 (1893) (2) Elbs, Kratz, *J. prakt. Chem.* (2) 55, 502-505 (1897). (3) Gibson, *Proc. Roy. Soc. Edinburgh* 44, 11 140-152 (1924); *C.A.* 18, 3041 (1924). (4) Fichter, Fritsch, Müller, *Helv. Chim. Acta* 6, 506 (1933). (5) Jaeger, *Cent.* 1912, I 1817.

3:0300 2-CHLOROBIPHENYL   $C_{12}H_9Cl$  Beil. V - 579  
(2-Chloro-xenene (1))  $Cl$  V<sub>1</sub>-(272)  
V<sub>2</sub>-(483)

M.P. 34° (2) (3) (4) (5) B.P. 273.7-273.8° at 738 mm. (7)  
33° (6) 267-268° (2)  
32.2° (7) 210-211° at 150 mm. (8)  
31° (15) 165-170° at 28 mm. (3)  
154° at 12.5 mm. (15)  
150-155° at 10 mm. (5)

Cryst. from alc. — Volatile with steam (6). — Sol. alc.,  $CCl_4$  (7); very sol.  $C_6H_6$  or pet. eth. (2).

[For prepn. (36.8% yield (7)) (together with other products) from biphenyl by direct chlorination in presence of Fe or other cat. see (7) (2) (8) (9); for prepn. (25-38% yield (5)) from diazotized *o*-chloroaniline +  $C_6H_6$  see (5) (4); for prepn. (60% yield (15)) from diazotized *o*-aminobiphenyl via  $Cu_2Cl_2$  method see (15) (10).]



[ $\bar{C}$  with  $C_6H_6 + AlCl_3$  in  $CS_2$  gives (37) (38) (39) (41) (by combined ring closure and addition to the unsatd. linkage or vice versa) 3-phenylhydrindone-1 (3-phenylindanone-1) [Beil. VII-483, VII<sub>1</sub>-(265)], cryst. from MeOH, m.p. 78° (37), 77-78° (39) (oxime, m.p. 141° (40), phenylhydrazone, m.p. 130° (40), *p*-nitrophenylhydrazone, m.p. 220-221° (39), semicarbazone, m.p. 223-225° (39)), accompanied by  $\beta,\beta$ -diphenyl-propionophenone (1,3,3-triphenylpropanone-1) [Beil. VII-524, VII<sub>1</sub>-(293)] (38) and other prods.: note that under similar condns (41) with toluene or *o*-xylene neither of the corresp. indanones is formed (see also below); however,  $\bar{C} + m$ -xylene +  $AlCl_3$  in  $CS_2$  yields (41) 5,7-dimethyl-3-phenylindanone-1, m.p. 101° (semicarbazone, m.p. 195-197° (41)), and  $\bar{C} + p$ -xylene +  $AlCl_3$  in  $CS_2$  yields (41) 4,7-dimethyl-3-phenylindanone-1, m.p. 94-95° (oxime, m.p. 218-219°; phenylhydrazone, m.p. 193-194°; semicarbazone, m.p. 232° (41)).]

[ $\bar{C}$  with many arom. epds. in pres. of  $AlCl_3$  condenses with loss of HCl to yield corresp. benzalacetophenone (chalcone) derivs.:  $\bar{C}$  with  $C_6H_6 + AlCl_3$ , however, gives no (41) chalcone (see above);  $\bar{C}$  with toluene +  $AlCl_3$  yields (41) 4'-methylchalcone;  $\bar{C}$  with *o*-xylene +  $AlCl_3$  in  $CS_2$  gives (63% yield (41)) 2'-methylchalcone;  $\bar{C}$  with *m*-xylene +  $AlCl_3$  in  $CS_2$  yields (41) 3'-methylchalcone;  $\bar{C}$  with biphenyl +  $AlCl_3$  in  $CS_2$  yields (41) 4'-phenylchalcone, m.p. 155-156° (45), 165° (11)]

[Similar chalcone formation occurs w many arom. ethers; e.g.,  $\bar{C}$  with anisole +  $AlCl_3$  in  $CS_2$  gives (42) 4'-methoxychalcone [Beil. VIII-193, VIII<sub>1</sub>-(560)], m.p. 106-107° (42);  $\bar{C}$  similarly with phenetole gives (42) 4'-ethoxychalcone [Beil. VIII-193], m.p. 74-75° (42);  $\bar{C}$  similarly with methyl *p*-tolyl ether gives (43) not only 2'-methoxy-5'-methylchalcone, m.p. 55-56°, but also by demethylation 2'-hydroxy-5'-methylchalcone, m.p. 111° (43);  $\bar{C}$  similarly with methyl 3,4-dimethylphenyl ether yields (13) 4',5'-dimethyl-2'-methoxychalcone, m.p. 78° (13);  $\bar{C}$  similarly with methyl  $\beta$ -naphthyl ether yields (44)  $\beta$ -methoxynaphthochalcone, m.p. 138-140° (44);  $\bar{C}$  similarly with diphenyl ether yields (37) 4'-phenoxychalcone, m.p. 85° (37); for extension of this reactn. to ethers of polyhydric phenols such as  $\bar{C} + AlCl_3 +$  catechol dimethyl ether (veratrole) (1:7560) (44), resorcinol dimethyl ether (1:7570) (13), resorcinol diethyl ether (1:7585) (13) (43), hydroquinone diethyl ether (1:7185) (43), and pyrogallol trimethyl ether (1:7145) (44) see indic. refs.]

[Similar formation of substituted chalcones occurs with  $\bar{C} + AlCl_3 +$  phenols; e.g., for cases of  $\bar{C}$  with *o*-cresol (1:1400) (46), resorcinol (1:1530) (47), phloroglucinol (1:1620) (47) cf. (48) see indic. refs.]

[ $\bar{C}$  with diazomethane in ether gives (49) (50) (note both replacement of Cl and addn. to unsatd. linkage) 5-(diazooacetyl)-4-phenylpyrazoline, cryst. from  $C_6H_6 +$  pet. eth.; m.p. 80-81° (49), 77-78° (50)]

[ $\bar{C} + NaN_3$  in ether gives (12% yield (51)) (52) cinnamoyl azide, cryst. from lgr., m.p. 86° dec. (51) (52); this cpd. on htg above m.p. or preferably in  $C_6H_6$  readily loses  $N_2$  and rearr. giving (77% yield (53)) (51) (52) styryl isocyanate, b.p. 107° at 12 mm.; this isocyanate (or even its azide precursor) with aq. at 50° yields (51) *N,N'*-distyrylurea, m.p. 213-214° (51); for its reactn. with MeOH yielding (52) methyl *N*-styrylcarbamate, m.p. 126°, with EtOH yielding (52) ethyl *N*-styrylcarbamate, m.p. 87°, with ammonia gas in dry ether yielding (51) *N*-styrylurea, m.p. 143°, or with aniline yielding (52) *N*-phenyl-*N*-styrylurea, m.p. 217°, see indic. refs.]

[ $\bar{C}$  with free  $NH_2OH$  in  $C_6H_6$  gives (100% yield (16)) cinnamoylhydroxamic acid, cryst. from hot EtOAc by addn. of lgr., m.p. 119.5° (16), 111.5° (54)]

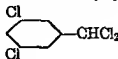
[ $\bar{C}$  htd. with urea at 70° gives (44% yield (55)) (56) *N*-cinnamoylurea, m.p. 208-209° (55), 197° (56).]

[For reactn. of  $\bar{C}$  with  $C_6H_5MgBr$  see (58); for reactn. of  $\bar{C}$  with cellulose see (59); for reactn. with *o*-aminothiophenol yielding 1-styrylbenzothiazole see (60); for reactn. of  $\bar{C}$



3:0360 (1) Hinkel, Hey, *J. Chem. Soc.* 1928, 2786-2791, (2) Scarborough, Waters, *J. Chem. Soc.* 1927, 93.

3:0370 3,5-DICHLOROBENZAL (DI)CHLORIDE  $C_7H_4Cl_4$  Beil. S.N. 466



M.P. 36.5° (1)

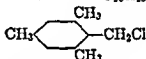
Colorless cryst. from MeOH or from dil. AcOH; eas. sol. usual org. solv. [Note that  $\bar{C}$  has same m.p. as the closely related 3,5-dichlorobenzyl chloride (3:0350) but that a mixture of the two becomes liquid.]

[For prepn. of  $\bar{C}$  from 3,5-dichlorobenzaldehyde (3:1475) with  $PCl_5$  (80% yield) see (1).]

$\bar{C}$  on hydrolysis with fuming  $H_2SO_4$  as directed gives (71-80% yield (1)) 3,5-dichlorobenzaldehyde (3:1475) (for study of rate of hydrolysis in 50% alc. at 83.5° see (2)).

3:0370 (1) Asinger, Lock, *Monatsh.* 62, 347 (1933). (2) Asinger, Lock, *Monatsh.* 62, 337-338 (1933).

3:0372 2,4,6-TRIMETHYLBENZYL CHLORIDE  $C_{10}H_{13}Cl$  Beil. S.N. 469  
( $\alpha^2$ -Chloroisodurene)



M.P. 37° (1) (2) (3) (4) B.P. 130-131° at 22 mm. (1)  
121-123° at 19 mm. (2)  
119° at 15 mm. (4)  
114-115° at 10 mm. (3)

[See also the isomeric 2,4,5-trimethylbenzyl chloride (3:9702).]

Colorless cryst. from alc. (4). —  $\bar{C}$  hlisters skin (3). — [Equiv. conductance of  $\bar{C}$  in liq.  $SO_2$  is 10 times that of benzyl chloride (3:8535) (3) cf. (5).]

### PREPARATION OF $\bar{C}$

[For prepn. of  $\bar{C}$  from 1,3,5-trimethylbenzene (mesitylene) (1:7455) with formalin (1:0145) + conc. HCl + HCl gas at 55° for 5½ hrs. (yields: 55-61% (1), 29% (3)) (some  $\alpha^2, \alpha^4$ -dichloropentamethylbenzene = bis-1,3-(chloromethyl)2,4,6-trimethylbenzene, cryst. from pet. eth., m.p. 105° (1) (3), is also formed) see indic. refs.]

[For prepn. of  $\bar{C}$  from mesitylene (1:7455) with chloromethyl methyl ether (3:7085) +  $SnCl_4$  (yields: 60% (4) cf. (6)), or in AcOH without other cat. (yields: 80-85% (7), 80% (2)), or with chloromethyl ethyl ether (3:7195) +  $SnCl_4$  in  $CCl_4$  soln. at -5° (70% yield (8)), see indic. refs.]

### CHEMICAL BEHAVIOR OF $\bar{C}$

Reduction. [ $\bar{C}$  with  $H_2$  + Pt cat. in alc. soln. gives (80% yield (2) cf. (7)) 1,2,3,5-tetramethylbenzene (isodurene) [Beil. V-430, V<sub>2</sub>(329)] (9), liquid, b.p. 195-197° at 760 mm., f.p. -24°,  $D_4^{20} = 0.8906$ .]

Hydrolysis.  $\bar{C}$  on hydrolysis (no details (2)) gives 2,4,6-trimethylbenzyl alc. (mesitylcarbinol), ndls. from alc., m.p. 89° (2), 88-89° (10) (3) (11), 87° (12) (corresp. *N*-phenylcarbamate, m.p. 124-125° (11)).

Conversion to ethers.  $\bar{C}$  with MeOH/KOH at 100° for 3 hrs. gives (70% yield (3)) methyl 2,4,6-trimethylbenzyl ether, oil, b.p. 109–110° nt 15 mm. (3),  $\bar{C}$  with EtOH/KOH similarly gives (77% yield (3)) ethyl 2,4,6-trimethylbenzyl ether, oil, b.p. 114–115° at 14 mm. (3).]

Conversion to esters.  $\bar{C}$  with AgOAc in AcOH nt 100° for 3 hrs. gives (70% yield (3)) 2,4,6-trimethylbenzyl acetate, oil, b.p. 136–137° at 15 mm. (3); this ester on hydrolysis with 15% aq. KOH at 100° for 3 hrs. gives (91% yield (3)) 2,4,6-trimethylbenzyl alc., m.p. 88–89°. (See also above.)]

Conversion to nitrile.  $\bar{C}$  in alc. with aq. NaCN (1) (13) or KCN (4) (8), or C with CuCN in pyridine (14) cf. (1), gives (yields: almost 100% (13), 89–93% (1)) mesitylacetoneitrile, cryst. from pet. eth., m.p. 79–80° (1), 79° (4); b.p. 160–165° at 22 mm. (13), 150–155° at 15 mm. (4), 190° at 11 mm. (8); this nitrile on hydrolysis with abt. 50% H<sub>2</sub>SO<sub>4</sub> under reflux for 6 hrs. gives (87% yield (1)) mesitylacetic acid [Beil. IX-563, IX<sub>1</sub>-(219)], cryst. from dil. alc. or lgr., m.p. 167–168° (1) (note that partial hydrolysis may give mesitylacetamide, m.p. 216° (8)).

#### BEHAVIOR OF $\bar{C}$ WITH ORGANOMETALLIC COMPOUNDS

With MeMgI.  $\bar{C}$  with MeMgI in dry ether undergoes mainly a coupling reaction giving (86% yield (15)) 1,2-dimesitylethane, m.p. 117.0–117.5°, accompanied by a little ethylmesitylene (1-ethyl-2,4,6-trimethylbenzene), b.p. 212–214° (15), 210° at 725 mm. (16),  $D_{20}^{20} = 0.894$  (16),  $n_D^{20} = 1.5074$  (16) (corresp. dinitro deriv., m.p. 111° (17), 109–111° (17) (15)).]

With misc. reactants.  $\bar{C}$  with diethyl sodiomalonate gives (4) diethyl  $\alpha$ -(2,4,6-trimethylbenzyl)malonate, m.p. 36°, b.p. 195–197° at 15 mm. (4). —  $\bar{C}$  with ethyl sodio-benzoylacetate gives (21% yield (18)) ethyl  $\alpha$ -(2,4,6-trimethylbenzyl)benzoylacetate which upon alk. hydrolysis gives (45% yield (18)) the ketone 1-benzoyl-2-mesitylethane, ndls. from MeOH, m.p. 85.0–85.5° (18).]

#### OTHER REACTIONS OF $\bar{C}$

$\bar{C}$  (1 mole) with hexamethylenediamine (1 mole) in CHCl<sub>3</sub> refluxed 3 hrs. gives (96% yield (19)) corresp. quaternary salt,  $\bar{C}_6H_{12}N_4$ : this prod. in nq. refluxed 4 hrs does not give the expected mesitaldehyde but instead (75% yield (19)) di-(2,4,6-trimethylbenzyl-amino)methane, cryst. from alc., m.p. 151.5–152° (19) ]

⑩ *N*-(2,4,6-Trimethylbenzyl)phthalimide: ndls. from alc., m.p. 209.5–210° (19). [*From*  $\bar{C}$  with K pbthalamide at 170–180° for 4 hrs. as directed (19) (63% yield (19)).]

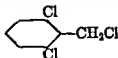
3:0372 (1) Fuson, Rabjohn, *Org. Syntheses* 25, 65–68 (1945). (2) *Monatsh.* 64, 412 (1934). (3) Nauta, *Diensk chim.* (5) 6, 1025–1033 (1939). (4) Hoch, *Compt. rend.* 192, 1465–1466 (1931). (5) (6) Sommelet, *Compt. rend.* 167, 1443 (1913). (7) (1937). (8) Sordes, *Compt. rend.* 195, 248–249 (1932 (1st ed.)), 360–362 (1943); 11, 66–69 (1931). (10) Fuson, Southwick, Rowland, *J. Am. Chem. Soc.* 66, 1112 (1944).

(11) Carre, *Bull. soc. chim.* (4) 7, 842–843 (1910). (12) Bock, Lock, Schmidt, *Monatsh.* 64, 412 (1934). (13) Fuson, Corse, McKeever, *J. Am. Chem. Soc.* 62, 3250 (1940). (14) Newman, *J. Am. Chem. Soc.* 59, 2472 (1937). (15) Fuson, Denton, Kneisley, *J. Am. Chem. Soc.* 63, 2652–2653 (1941). (16) Smith, Kiess, *J. Am. Chem. Soc.* 61, 285–286 (1939). (17) Smith, Kiess, *J. Am. Chem. Soc.* 61, 995–996 (1939). (18) Fuson, Ulyott, Hickson, *J. Am. Chem. Soc.* 61, 410–411 (1939). (19) Fuson, Denton, *J. Am. Chem. Soc.* 63, 654–656 (1941).

1932, II 2371. (15) Bertozzi, *Gazz. chim. ital.* **29**, II 37-38 (1899).

### 3:0410 2,6-DICHLOROBENZYL CHLORIDE

$C_7H_5Cl_3$  Beil. S.N. 466



M.P. 39-40° (1)

Colorless cryst. from lgr., ether, or alc. + ether.

[For prepn. of  $\bar{C}$  from 2,6-dichlorotoluene (3:6270) by treatment at h.p. with  $Cl_2$  in u.v. light see (1).]

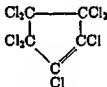
$\bar{C}$  with Mg in dry ether gives 90% yield 2,6-dichlorobenzyl MgCl; this prod. upon treatment with  $CO_2$  (1) or with methyl chloroformate (3:5075) followed by appropriate treatment yields 2,6-dichlorophenylacetic acid, cryst. from alc., m.p. 157-158° (1).

3:0410 (1) Austin, Johnson, *J. Am. Chem. Soc.* **54**, 658-659 (1932).

### 3:0422 OCTACHLOROCYCLOPENTENE

$C_5Cl_8$

Beil. V - 62



V<sub>1</sub>—  
V<sub>2</sub>—

M.P.

B.P.

41° (1) (8)	283-284° at 733 mm. (5) (6)	$D_4^{50} = 1.817$ (4)	$n_D^{50} = 1.5660$ (4)
40-41° (7)	283° (1)		
40° (2)	183° at 20 mm. (2)		
39° (3)	140° at 10 mm. (4)		
38° (4)			
32° (10)			

[See also hexachlorobutadiene-1,3 (3:6425).]

Colorless cryst. from 95% alc. (4) or EtOH contg. 5% tetrachloroethylene (3:5460) (3).

[For prepn. of  $\bar{C}$  from pentachlorocyclopentenone [Beil. VII-49] (7), from either the higher- or lower-melting stereoisomer of hexachlorocyclopentenone [Beil. VII-49] (1), from dibromo-dichloro-cyclopentanetrione [Beil. VII-853] (8), or from xanthogallol (tetrabromocyclopentenedione [Beil. VII-(321)] (2), all with  $PCl_5$  in s.t., at elevated temps. as directed, see indic. refs.]

[For formn. from nonachloropentene-1 (itself obtd. from hexachloropropene (3:6370) with trichloroethylene (3:5170) +  $AlCl_3$  (9)) by elimination of 1 HCl with alc. KOH yielding octachloropentadiene-1,3 followed by rearr. to  $\bar{C}$  by hoilg. with  $AlCl_3$  see (3).]

[For formn. of  $\bar{C}$  (together with  $CCl_4$  (3:5100) and hexachloroethane (3:4835) by high-press./high-temp. chlorination of chloropentanes see (4); by exhaustive chlorination of hexyl iodide, heptaldehyde, heptylic acid, etc. (5), of high-mol.-wt. hydrocarbons (6), or of 3-chloro-5,6-dihydroxy-2-(dichloromethyl)pyridine [Beil. XII-164] (10), see indic. refs.]

Note that  $\bar{C}$ , formerly regarded as hexachlorobutadiene-1,3 (3:6425), is currently (3) believed to have the structure octachlorocyclopentene; for Raman spectra evidence see (11).

3:0422 (1) Zincke, *Küster, Ber.* 23, 2214-2215 (1890). (2) Hantzsch, Strasser, *Ann.* 488, 209 (1891). (3) McBee, Hass, Pierson, *Ind. Eng. Chem.* 803-806 (1877). (6) Hartmann, *Ber.* 24, 1011-1026 (1891). (7) *Ann.* 352, 52-53 (1907). (9) Hoffmann, *Ber.* 22, 1269-

### 3:0425 2,3,4-TRICHLOROTOLUENE


 $C_7H_5Cl_3$ 
*Beil.* V - 298

 $V_1$ —

 $V_2$ -(232)

M.P. 41° (1) (2) (3) B.P. 231-232° at 716 mm. (1)  
40-41° (4)

Ndls. from MeOH or EtOH; volatile with steam.

[For prepn. of  $\bar{C}$  from 2,3-dichloro-4-aminotoluene (*Beil.* XII-990) via diazotization and use of  $Cu_2Cl_2$  reaction see (4); from toluene with  $AlCl_3 + SO_2Cl_2$  (34%  $\bar{C}$  + 40% 2,4,5-trichlorotoluene (3:2100)) see (2); for formn. of  $\bar{C}$  (together with other isomers) from toluene, *o*-chlorotoluene (3:8245), or *p*-chlorotoluene (3:8287) with  $Cl_2$  see (1), from 2,3-dichlorotoluene (3:6345) or 2,4-dichlorotoluene (3:6290) with  $Cl_2$  in pres. of  $Al/Hg$  see (5); for prepn. of  $\bar{C}$  from its sulfonic acid by hydrolysis see (1) (7).]

[ $\bar{C}$  with  $Cl_2$  in pres. of  $Al/Hg$  yields (6) 2,3,4,6-tetrachlorotoluene (3:2450).]

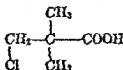
$\bar{C}$  on mononitration (1) (4) by soln. in cold fuming  $HNO_3$  yields a mononitro  $\bar{C}$  (*Beil.* V-333), ndls. from alc., m.p. 60-61° (4), 60° (1);  $\bar{C}$  on dinitration by warming with a mixt. of 2 pts. fuming  $HNO_3$  and 1 pt. conc.  $H_2SO_4$  (1) (4) cf. (7) yields 2,3,4-trichloro-5,6-dinitrotoluene [*Beil.* V-345], ndls. from alc., m.p. 141° (1) (2), 140-141° (4).

$\bar{C}$  on shaking with 2 pts. fuming  $H_2SO_4$  at 60° yields (1) (7) a monosulfonic acid (use in sepn. of  $\bar{C}$  from 2,4,5-trichlorotoluene (3:2100) which is not sulfonated under these conditions (1) (7)).

$\bar{C}$  on oxidn. with dil.  $HNO_3$  in s.t. at 150° (4) yields 2,3,4-trichlorobenzoic acid (3:4810), m.p. 186-187° (4).

3:0425 (1) Seelig, *Ann.* 237, 132, 137, 138, 140, 156 (1887). (2) Silberrad, *J. Chem. Soc.* 127, 2681-2682 (1925). (3) I G., *Brit.* 287,178, May 9, 1928, *Cent.* 1929, II 352. (4) Cohen, Dakin, *J. Chem. Soc.* 81, 1327-1328 (1902). (5) *Ref.* 4, pp. 1339-1341. (6) Cohen, Dakin, *J. Chem. Soc.* 83, 1283 (1904). (7) Prentzell, *Ann.* 296, 181-182 (1897).

### 3:0440 CHLOROPIVALIC ACID ( $\beta$ -Chloro- $\alpha,\alpha$ - dimethylpropionic acid)

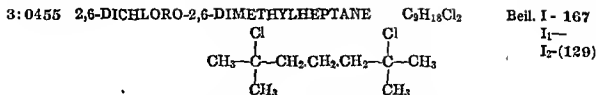

 $C_6H_9O_2Cl$ 
*Beil.* S.N. 162

M.P. 40-42° (1) B.P. 126-129° at 30 mm. (1)

[For prepn. of  $\bar{C}$  from pivalic acid (trimethylacetic acid) (1:0410) with  $SO_2Cl_2$  + dibenzoyl peroxide in  $CCl_4$  see (1).]

Ⓒ Chloropivalamide: pl. from aq., m.p. 108-109° (1).

3:0440 (1) Kharasch, Brown, *J. Am. Chem. Soc.* 62, 925-929 (1940). (2) Kharasch, Brown (to du Pont Co.), U.S. 2,302,228, Nov. 17, 1942; *C.A.* 37, 2018 (1943).



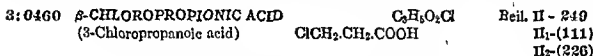
M.P. 41-42° (1)

[For prepn. of  $\bar{C}$  from 2,6-dimethylheptanediol-2,6 [Beil. I-494] (2) with conc. HCl or AcCl see (1) (2); from the corresponding internal ether, viz.,  $\alpha, \alpha, \alpha', \alpha'$ -tetramethylpentamethylene oxide (2,2,6,6-tetramethyltetrahydropyran) [Beil. XVII-17], with HCl see (1).]

$\bar{C}$  on warming with aq. readily hydrolyzes (1) back to 2,6-dimethylheptanediol-2,6 (monohydrate, cryst. from  $C_6H_6$ , m.p. 60-61°; anhydrous form by heating monohydrate at 135-140°, m.p. 76-77° (1)).

[ $\bar{C}$  in  $C_6H_6$  + AcOH treated with Zn dust in a stream of dry HCl yields (2) mixt. of  $\alpha$ - and  $\beta$ -cyclogeraniols [Beil. VI-66, VI-(43)].]

3:0455 (1) Bruylants, *Bull. acad. roy. Belg.* 1909, 276-282; *Cent.* 1909, II 797; *C.A.* 4, 1485 (1910); *Rec. trav. chim.* 29, 130-133 (1910). (2) Staudinger, Widmer, *Helv. Chim. Acta* 9, 531, 546-547 (1926).



M.P. 42°	(1) (2)	B.P. 204°	(11)
41.5°	(3)	203-205° at 764 mm.	(12)
41°	(4) (19)	127° at 35 mm.	(13)
40.5° cor.	(5)	120° at 30 mm.	(27)
40°	(6) (7)	124° at 25 mm.	(1)
39°	(8) (9)	105-107° at 20 mm.	(14)
38.5-39.5°	(10)	108° at 12 mm.	(1)

Lfts. from lgr. or pet. eth. — Very eas. sol. aq., alc.,  $CHCl_3$ ; spar. sol. dry ether. — Fairly, hygroscopic. —  $\bar{C}$  on boilg. slightly dec. to HCl + acrylic ac. (1:1020). [Note that samples with m.p. higher than 42° may have contd. adipic ac. (8).] [For stability of  $\bar{C}$  in aq. soln. see (8).]

[For prepn. of  $\bar{C}$  from acrolein (1:0115) via addn. of HCl to  $\beta$ -chloropropionaldehyde (3:5576) and subsequent oxidn. with fuming  $HNO_3$  (yield: 65-70% (14), 60-65% (15), 50% (1)) see (15) (14) (7) (1) (16); from 3-chloropropanol-1 (trimethylene chlorohydrin) (3:8285) by oxidn. with conc.  $HNO_3$  (yield: 78-79% (9)) (17) (13) (27) or alk.  $KMnO_4$  (18) see indic. refs.; from  $\beta$ -hydroxypropionitrile (ethylene cyanohydrin) by hydrolysis with HCl see (10); from phosgene + ethylene +  $AlCl_3$  via hydrolysis of intermediate  $\beta$ -chloropropionyl chloride (3:5690) see (19); for other methods see Beil. II-249.]

$\bar{C}$  on htg. with aq. alk. or alk. carbonates (1) (7) (19) or on passing over activated carbon at 230-240° at 250-320 mm. (21) loses HCl and yields acrylic ac. (1:1020). [The alk. salts of  $\bar{C}$  dec. even at ord. temp. giving alk. chlorides (3).] [For example of use of  $\bar{C}$  as source of acrylic acid in Diels-Alder addn. reactions see under 9,10-dichloroanthracene (3:4916).]

$\bar{C}$  with  $PCl_3$  (12) or  $SOCl_2$  (22) yields  $\beta$ -chloropropionyl chloride (3:5690) q.v., b.p. 144°.

$\bar{C}$  (1 g.) + pyridine (2 g.) htd. at 100° solidifies after 2 hrs. to give 100% yield addn. cpd.  $\bar{C}.C_5H_5N$ , pr. from abs. alc., m.p. 160° (26).

— Methyl  $\beta$ -chloropropionate: b.p. 148–150° at 760 mm. (3:5765)

— Ethyl  $\beta$ -chloropropionate: b.p. 162–163° at 760 mm. (3:8290).

—  $\beta$ -Chloropropionamide: unrecorded.

①  $\beta$ -Chloropropionanilide: cryst. from aq. or MeOH, m.p. 119° (23). [From  $\beta$ -chloropropionyl chloride + aniline in acetone in 90% yield (23).]

②  $\beta$ -Chloropropion-*p*-toluidide: cryst. from MeOH, m.p. 121° (23) (22).

③  $\beta$ -Phenoxypropionic acid: ndls. from bot aq. (24) or lgr. (25); m.p. 98° (24), 97–98° (25). [From  $\bar{C}$  + phenol + NaOH, 36% yield (25).]

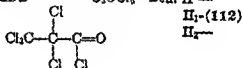
3:0460 (1) Moureu, Murst, Tampier, *Ann. chim.* (9) 15, 222–228 (1921). (2) Wooten, Hammett, *J. Am. Chem. Soc.* 57, 2291 (1935). (3) Beckurts, Otto, *Ber.* 18, 226, 846 (Note) (1885). (4) Michael, *Ber.* 34, 4047–4048 (1901). (5) Linnemann, *Ann.* 163, 96 (1872). (6) Lichty, *Ann.* 319, 369–379 (1901). (7) Moureu, *Ann. chim.* (7) 2, 157–158 (1894); *Bull. soc. chim.* (3) 9, 388 (1893). (8) Simpson, *J. Am. Chem. Soc.* 40, 675 (1918). (9) Powell, Huntress, Hershberg, *Org. Syntheses*, Coll. Vol. 1 (2nd ed.), 168–169 (1941). (10) Jacobs, Heidelberger, *J. Am. Chem. Soc.* 39, 1465–1466 (1917).

(11) de Barr, *Am. Chem. J.* 22, 334 (1899). (12) Henry, *Compt. rend.* 109, 114 (1885); *J. prakt. Chem.* (2) 31, 126 (1885). (13) Powell, *J. Am. Chem. Soc.* 46, 2879 (1924). (14) Moureu, Chaux, *Bull. soc. chim.* (4) 35, 1360–1364 (1924). (15) Moureu, Chaux, *Org. Syntheses*, Coll. Vol. 1 (2nd ed.), 166–168 (1941). (16) Arndt, *Ber.* 56, 1276–1277 (Note) (1923). (17) Rojahn, *Ber.* 54, 3116–3117 (1921). (18) Brit. (to I.G.I.), 479,690, Mar. 19, 1938; *Cent.* 1938, I 3833; French 824,483, Feb. 9, 1938; *C.A.* 32, 5857 (1938). (19) Pace, *Gazz. chim. ital.* 59, 580–582 (1929). (20) Klebanskii, Chevychalova, *Cent.* 1938, I 1335, *C.A.* 34, 6222 (1940).

(21) Bauer, Lauth (to Rohm and Haas Co.), U.S. 2,087,466, July 20, 1937; *Ger.* 646,820, June 23, 1937; *Cent.* 1937, II 2072, *Brit.* 526,122, Sept. 11, 1910, *C.A.* 35, 6981 (1941). (22) Wolfenstein, Rolle, *Ber.* 41, 736 (1908). (23) Mayer, van Zutphen, Philipps, *Ber.* 58, 860 (1927); Mayer, *Ger.* 415,096, June 13, 1925, *Cent.* 1925, II 1094. (24) Powell, *J. Am. Chem. Soc.* 45, 2710 (1923). (25) Arndt, Kallner, *Ber.* 57, 204 (1924). (26) Kirpal, Wojnar, *Ber.* 71, 1264 (1938). (27) Fieser, Seligman, *J. Am. Chem. Soc.* 58, 2484 (1936).

### 3:0470 PENTACHLOROPROPIONYL CHLORIDE

$C_3OCl_5$  Beil. II —



M.P. 42° (1)

Colorless not especially hygroscopic ndls.

[For prepn. of  $\bar{C}$  from trichloroacrylic acid chloride (3:5845) by addn. of  $\text{Cl}_2$  in bright sunlight see (1).]

$\bar{C}$  with  $\text{AlCl}_3$  (1 mole) at 60° decomposes in two ways (1), leading on one hand to CO and hexachlorethane (3:4835), and on the other to phosgene (3:5000) and tetrachloroethylene (3:5460).

[ $\bar{C}$  with  $\text{C}_6\text{H}_6$  +  $\text{AlCl}_3$  yields (1) pbenyl pentachloroethyl ketone ( $\alpha,\alpha,\beta,\beta,\beta$ -pentachloropropiophenone) (Beil. VII<sub>1</sub>-(161)), m.p. 83° (1).]

$\bar{C}$  on hydrolysis yields pentachloropropionic acid (3:4895).

3:0470 (1) Böeseken, Hasselbach, *Rec. trav. chim.* 32, 11–13 (1913).

3:0475 *p*-CHLOROPHENOL $\text{C}_6\text{H}_5\text{OCl}$ 

Beil. VI - 186

VI<sub>1</sub>-(100)VI<sub>2</sub>-(174)

M.P.

B.P.

43° (1) 219.75° at 760 mm. (11)  $D_4^{28.1} = 1.2238$  (22)

42.9° (2) (3) 218.3-218.9° (12)

 $n_D^{65} = 1.5480$  (23)

42.5° (4) 218° (6) (15)

 $n_D^{40} = 1.5600$  (14)

40-41° (5) 217° at 760 mm. (7)

1.5570 (3)

41° (6) (15) 217° (10)

 $n_D^{20} = 1.5690$  (14)

40° (7) 216.0° at 760 mm. (13)

38-39° (8) 99.7° at 12 mm. (13)

37° (9) (10) (20) (55)

36° (39)

[See also *o*-chlorophenol (3:5980).]

$\bar{C}$  has disagreeable and persistent odor (15) for study of strength of which in aq. soln. see (16). —  $\bar{C}$  is spar. sol. aq. at ord. temp. (for details see (17)); but  $\bar{C}$  is eas. sol. alc., ether,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ ,  $\text{CS}_2$ . —  $\bar{C}$  (like its *o*-isomer (3:5980)) is volatile with steam (for studies see (18)) even from soln. in equiv. aq.  $\text{NaOH}$  (19) (dif. and sepn. from 2,4-dichlorophenol (3:0560), 2,6-dichlorophenol (3:1595), and 2,4,6-trichlorophenol (3:1673) (19).

The cryoscopic const. of  $\bar{C}$  is 85.8 (20).

SELECTED DATA ON BINARY SYSTEMS CONTG.  $\bar{C}$ 

$\bar{C}$  + aq.: for solubility/temp. data see (17).

$\bar{C}$  +  $\text{C}_6\text{H}_6$ : for solubility/temp. data (17) or for vapor-press. data (21) see indic. refs.; for association of  $\bar{C}$  in  $\text{C}_6\text{H}_6$  soln. see (30).  $\bar{C}$  +  $\text{MeOH}$  (1:6120): for vapor-press. data see (21).  $\bar{C}$  + acetone (1:5400): for vapor-press. data see (21).  $\bar{C}$  + methyl acetate (1:3005): for vapor-press. data see (21).

$\bar{C}$  + nitrobenzene: for f.p./compn. data and diagrams see (24) (25), eutectic m.p.  $-24.5^\circ$  contg. 41.5 wt. %  $\bar{C}$  (24), m.p.  $-30.5^\circ$  contg. 60.5 mol. %  $\bar{C}$  (25).

$\bar{C}$  + aniline: for  $D^{25}$  and  $D^{50}$  + viscosity nt 25° and 50° see (26).  $\bar{C}$  + *p*-toluidine: for f.p./compn. and  $n_D^{54}$ /compn. data and diagrams see (4) cf. (29); note two eutectics,  $E_1$ , m.p.  $21^\circ$  contg. 28 mol. %  $\bar{C}$ , and  $E_2$ , m.p.  $7.4^\circ$  contg. 71 mol. %  $\bar{C}$  (4).  $\bar{C}$  + benzylamine: for f.p./compn. diagram see (27), noting two molecular cpds., one of compn. 3  $\bar{C}$ :1 benzylamine, m.p.  $55^\circ$ , the other 1  $\bar{C}$ :1 benzylamine, m.p.  $16^\circ$  (27).  $\bar{C}$  + phenylhydrazine: for f.p./compn. data and diagram see (1).

$\bar{C}$  + piperidine: for  $n_D^{55}$ /compn. data see (23).

$\bar{C}$  + pyridine: for f.p./compn. diag. of entire system see (4) cf. (28) (note two eutectics, viz.,  $E_1$ , m.p.  $-19.5^\circ$  contg. 66.6 mol. %  $\bar{C}$ ,  $E_2$ , m.p.  $-47.3^\circ$  contg. 13.5 mol. %  $\bar{C}$ ); for  $n_D^{25}$ /compn. and  $n_D^{50}$ /compn. data over entire system see (14).

$\bar{C}$  + *o*-chlorophenol (3:5980): for f.p./compn. data and diagram see (3) (note that the eutectic, m.p. about  $-20.5^\circ$ , conts. about 33.5 mol. %  $\bar{C}$ ).  $\bar{C}$  + *p*-dichlorobenzene (3:0980): for f.p./compn. diagram see (4) (note eutectic m.p.  $27.2^\circ$  contg. 73.4 mol. %  $\bar{C}$ ); for  $n_D^{54}$ /compn. data see (4).

AZEOTROPIC SYSTEMS CONTG.  $\bar{C}$ 

$\bar{C}$  with naphthalene (1:7200) forms a const.-boilg. mixt., b.p.  $216.3^\circ$  contg. 36.5%  $\bar{C}$  (11).  $\bar{C}$  with *p*-dibromobenzene forms a const.-boilg. mixt., b.p.  $215.05^\circ$  contg. 35%  $\bar{C}$  (11).

PREPARATION OF  $\bar{C}$ 

From *p*-chloroaniline. [For prepn. of  $\bar{C}$  from *p*-chloroaniline {Beil. XII-607, XII-1-(304)}] via diazotization to salts of *p*-chlorobenzenediazonium hydroxide {Beil. XVI-463, XVI-1-(355)} and hydrolysis of the latter (yields not stated) (3) (10) in an inert solvent (31) see indic. refs.; for study of rate of hydrolysis (32) of *p*-chlorobenzenediazonium chloride and influence of light thereon (33) see indic. refs.]

From phenol. [For prepn. of  $\bar{C}$  from phenol (1:1420) with  $Cl_2$  at temps. over range  $40^\circ$ - $155^\circ$  see (3) cf. (6) (35); with  $Cl_2$  + conc. aq.  $NH_2CO_2$  soln. see (34), by use of *N,N*-dichlorobenzenesulfonamide in  $CHCl_3$  at  $-15^\circ$  see (36) (note that evidence ohld. from this reaction in pres. of isobutylene indicates that phenyl hypochlorite is first formed and subsequently rearranges (36)); by use of *N,N*-dichlorourea +  $HCl$  see (37), with  $EtOCl$  (3:7022) in  $CCl_4$  at  $-20^\circ$  see (38); or by use of  $SO_2Cl_2$  see (39) (40) (41) (for use of  $SO_2Cl_2$  on  $NaOC_6H_5$  see (7)). — Note that in all these methods some *o*-chlorophenol (3:5980) is usually also formed.]

From *p*-aminophenol. [For formn. of  $\bar{C}$  from *p*-aminophenol {Beil. XIII-427, XIII-1-(143)}] via diazotization, conversion to corresp.  $PtCl_4$  double salt, and dry distn. see (42); or via diazotization, conv. to corresp.  $ZnCl_2$  double salt, and decompn. by addn. of molten phenol (yield 40% accompanied by 41% hydroxybiphenyl + 11% diphenyl ether) see (43).]

From *p*-dichlorobenzene. [For prepn. of  $\bar{C}$  from *p*-dichlorobenzene (3:0980) with  $MeOH/NaOMe$  in s.t. at  $180^\circ$  (44) (45), or with  $MeOH/NaOH$  in s.t. at  $190$ - $195^\circ$  (90% yield (46)) or at  $200^\circ$  for 25 hrs. under press. (8), see indic. refs.; for use of aq. alk. or alk. earths with  $MeOH$  in pres. of copper salts at  $150$ - $190^\circ$  under press. see (47) (note, however, that, although the hydrolysis of *p*-dichlorobenzene to  $\bar{C}$  is markedly facilitated by presence of  $Cu$ , e.g., with aq.  $NaOH$ , maximum yield is 30% while with  $MeOH/NaOH$  +  $Cu$  yield is 85% (48), yet in presence of  $Cu_2O$  some ord. phenol (1:1420) is also formed (49); for prepn. of  $\bar{C}$  from *p*-dichlorobenzene (3:0980) by vapor-phase hydrolysis with steam + cat. at  $550$ - $850^\circ$  see (50).]

From other miscellaneous sources. [For formn. of  $\bar{C}$  from various *p*-chlorophenyl ethers by cleavage, e.g., from *p*-chloroanisole (3:6300) with conc.  $HCl$  in s.t. (51) or with  $MeOH/NaOMe$  in s.t. at  $176^\circ$  (45); from *p*-chlorophenetole (3:0090) with conc.  $HCl$  (52) or with  $HBr$  in  $AcOH$  (85% yield (53)); or from *p*-chlorophenoxyacetic acid (3:4375) with conc.  $HCl$  in s.t. at  $150^\circ$  (34), see indic. refs.]

[ $\bar{C}$  is also obtainable by hydrolysis of its various esters, but these need not be cited here.]

[For formn. of  $\bar{C}$  from *p*-bromophenol with  $SO_2Cl_2$  at ord. temp. see (55); from calcium salt of *p*-dichlorobenzenesulfonic acid with  $Ca(OH)_2$  +  $Cu$  at  $200$ - $220^\circ$  followed by removal of the sulfonic acid group from the resultant *p*-chlorophenolsulfonic acid see (56).]

BIOCHEMICAL ASPECTS OF  $\bar{C}$ 

[For studies involving fate of  $\bar{C}$  in animal metabolism see (57) (58) (59); for studies from various aspects of bactericidal and fungicidal action of  $\bar{C}$  see (60) (61) (62) (63) (64) (65) (67) (68).]

[For studies from various aspects of effect of  $\bar{C}$  and other chlorophenols on taste of water see (69) (70) (71) (72) (73).]

MISCELLANEOUS USES OF  $\bar{C}$ 

[For use of  $\bar{C}$  in selective solv. refining of mineral oils see (74); as denaturant for alc. see (75); as solv. for lignin see (76).]



QUANT. DETN. OF  $\bar{C}$ 

See text below under bromination of  $\bar{C}$ , iodination of  $\bar{C}$ , and nitration of  $\bar{C}$ .

CHEMICAL BEHAVIOR OF  $\bar{C}$ PYROLYSIS OF  $\bar{C}$ 

[ $\bar{C}$  on pyrolysis through silica tube at red heat gives (77) 3,6-dichlorodiphenylene oxide, m.p. 188° (77).]

REDUCTION OF  $\bar{C}$ 

[ $\bar{C}$  with  $H_2 + Ni$  cat. in aq. or nq. alc. alk. soln. loses chlorine quant. as  $HCl$  (78) (for study of rate see (79)); note also that  $\bar{C}$  with  $Li$  at 220° (80) or with  $Ca$  at 160° (80) followed by treatment with aq. gives (yields 14% and 36% resp.) phenol (1:1420). — Note that  $\bar{C}$  with aq.  $Cu_2O$  at 250–380° under press. gives (81) phenol (1:1420) (see also above under prepn. of  $\bar{C}$  from *p*-dichlorobenzene). — Note that reduction of  $\bar{C}$  to 4-chlorocyclohexanol-1 (3:9376) appears to be unreported.]

OXIDATION OF  $\bar{C}$ 

[ $\bar{C}$  on oxidn. with 35% peracetic acid at 25° gives (82) slowly (17 days) in small yield  $\beta$ -chloromuconic acid (2-chlorobutadien-1,3-dicarboxylic acid-1,4), m.p. 223°, accompanied in the mother liquor by some lactone ( $C_6H_4O_3Cl$ ) of 3-chloro-4,5-dihydroxyhexen-2-dioic acid-1,6, m.p. 177° (82). —  $\bar{C}$  on electrolytic oxidn. gives (83) benzoquinone-1,4 (1:9025).]

NUCLEAR SUBSTITUTION OF  $\bar{C}$ 

(See also below under condensation reactions of  $\bar{C}$ .)

**Halogenation of  $\bar{C}$ . Fluorination.** [The fluorination of  $\bar{C}$  has not been reported, and no fluoro- or difluoroderiv. of  $\bar{C}$  is known.]

**Chlorination.** [ $\bar{C}$  with  $Cl_2$  (2 moles) in  $AcOH$  in cold gives (80% yield (84)) 2,4-dichlorophenol (3:0560), m.p. 45°; presumably  $\bar{C}$  with  $Cl_2$  (3 moles) would give 2,4,6-trichlorophenol (3:1673), but such reaction is not actually reported. — For study of rate of chlorination of  $\bar{C}$  with  $Cl_2$  in  $CCl_4$  (85) or with  $NaOCl$  in alk. soln. at 25° (86), or behavior of  $\bar{C}$  with  $Cl_2$  in presence of radioactive  $HCl$  in  $C_6H_6$  soln. (87), see indic. refs.]

**Bromination.** [ $\bar{C}$  with  $Br_2$  (1 mmole) in  $CCl_4$  at room temp. gives (62% yield (88)) 2-bromo-4-chlorophenol, m.p. 33–34°, h.p. 121–123° at 10 mm. (corresp. benzoyl deriv., m.p. 99–100°) (88).]

$\bar{C}$  with  $Br_2$  (2 moles) in  $AcOH$  (89) (90) (91) or  $\bar{C}$  with  $Br_2$  (2 moles) in aq.  $KBr$  soln. (92) gives (yields not stated) 4-chloro-2,6-dibromophenol, ndls. from dil. alc., m.p. 92° (89), 90° cor. (92), 89° (90) (corresp. methyl ether, m.p. 74° (92); 2,4-dinitrophenyl ether, m.p. 145–146° (90), *p*-toluenesulfonate, m.p. 107–108° (90)). [Note difference from the isomeric 4-chloro-3,5-dibromophenol, m.p. 121° (93), 118° (94) (corresp. Me ether, m.p. 82.5° (93), benzoyl deriv., m.p. 132° (94)).]

[ $\bar{C}$  with  $Br_2$  (4 moles) in pres. of  $Fe$  powder gives (93) 4-chloro-2,3,5,6-tetra bromophenol, m.p. 215° (corresp. methyl ether, m.p. 161°, benzoyl deriv., m.p. 203° (93)).]

[For quant. detn. of  $\bar{C}$  by bromination with  $KBrO_3/KBr$  soln. see (95) (96) (97).]

**Iodination.**  $\bar{C}$  with  $I_2$  (1 mole) in aq.  $KI + conc. NH_4OH$  gives (88% yield (98)) 4-chloro-2-iodophenol, ndls. from  $CHCl_3$  or lt. pet., m.p. 78° (98) (99) (corresp. acetyl deriv., m.p. 57° (98); corresp. benzoyl deriv., m.p. 88° (99), 83–84° (98); corresp. *N*-phenylcarbamate, m.p. 128° (99)).

$\bar{C}$  with excess  $I_2$  in aq.  $KI + conc. NH_4OH$  (98), or  $\bar{C}$  in alk. soln. with  $I_2$  in aq.  $KI$  (92),

or  $\bar{C}$  in alk. soln. with  $I_2 + KIO_3$  followed by dil  $H_2SO_4$  (89), or  $\bar{C}$  with  $ICl$  (99), gives (89% yield (98)) 4-chloro-2,6-iodophenol, ndls. from alc. or lt. pet., m.p.  $109^\circ$  cor. (92),  $108^\circ$  (98) (100),  $107-108^\circ$  (89),  $106-107^\circ$  (99) (corresp. methyl ether, m.p.  $79^\circ$  (92); corresp. acetyl deriv., m.p.  $128^\circ$  (98),  $127.5^\circ$  (100)).

[For quant. detn. of  $\bar{C}$  by di-iodination using  $I_2 +$  borax soln. : : Nitration of  $\bar{C}$ .  $\bar{C}$  on mononitration with 30%  $HNO_3$  in cold (103), or with nitric acid (105). (Beil. VI-238, 101) (102) (corresp. ethyl ether, m.p.  $61-62^\circ$  (101); cor. (99)). — [For use of mononitration in quant. detn. of m. o-chlorophenol (3:5980) see (107) of (112).]

$\bar{C}$  on dinitration with conc.  $HNO_3$  (108) (or the above 4-chloro-2-nitrophenol on further nitration with fuming  $HNO_3$  (101)) gives 4-chloro-2,6-dinitrophenol (Beil. VI-260, VI-128), yel. ndls. or lfts. from aq., ndls. or pr. from alc., ether, or  $CHCl_3$ , m.p.  $81^\circ$  (108) (corresp. methyl ether, m.p.  $66^\circ$  (109),  $64^\circ$  (94), corresp. ethyl ether, m.p.  $54-55^\circ$  (110); corresp. *N*-phenylcarbamate cannot be prepared (111)).

Nitrosation of  $\bar{C}$ . [Unlike the isomeric o-chlorophenol (3:5980) the nitrosation of  $\bar{C}$  has not been reported, and no nitroso-*p*-chlorophenol is known.]

Sulfonation of  $\bar{C}$ . [ $\bar{C}$  with equiv. amt. fuming  $H_2SO_4$  ( $D = 1.90$ ) at  $100^\circ$  (113) (114) gives 4-chlorophenolsulfonic acid-2 (Beil. XI-236), deliquescent tbs. of monohydrate from aq., m.p.  $75-76^\circ$  (113) (for study of acid strength see (115)) — Note also that  $\bar{C}$  with very large excess (15 wt. pts.) fuming  $H_2SO_4$  (20%  $SO_2$ ) gives (80-85% yield (116)) a bimolecular condensation prod. of the above sulfonic acid.]

Mercuration of  $\bar{C}$ . [ $\bar{C}$  with  $HgO/HgSO_4$  on warming, followed by neutraliz. with  $NaOH$ , gives (117) 4-chloro-2-hydroxymercuriphenol (Beil. XVI-(564)). — For other studies of mono- and di-mercuration of  $\bar{C}$  see (118) (119); for patents see (120) (121).]

#### CONDENSATION REACTIONS INVOLVING NUCLEAR HYDROGEN OF $\bar{C}$

With alcohols.  $\bar{C}$  with alcs. contg. more than one C in pres. of conc.  $HClO_4$  at  $0-160^\circ$  gives ultimately (although doubtless through formn. of intermediate esters followed by rearr. or intermediate formn. of olefins followed by addn.) (122) the corresp. 2-alkyl-4-chlorophenols [e.g.,  $\bar{C}$  with isopropyl alc. (1:6135) + conc.  $HClO_4$  as directed (122) gives 4-chloro-2-isopropylphenol, sol. aq.  $NaOH$ , b.p.  $235-250^\circ$  accompanied by 4-chloro-2,6-diisopropylphenol, insol. aq.  $NaOH$ , m.p.  $260-265^\circ$ ].

With aldehydes. [ $\bar{C}$  with formaldehyde (1:0145) + conc.  $HCl + H_2SO_4$  is claimed (123) to undergo simple chloromethylation yielding 5-chloro-2-hydroxybenzyl chloride, m.p.  $85^\circ$  (123); note, however, that further condensation (involving 2 additional moles of formaldehyde) may occur giving (67% yield (121)) 6-chloro-8-(chloromethyl)benzodioxane-1,3, cryst. from  $MeOH$ , m.p.  $103^\circ$  (124). —  $\bar{C}$  with formaldehyde (1:0145) + aq. alkali gives (125) 4-chloro-2,6-bis-(hydroxymethyl)phenol ("p-chlorophenol dialcohol"), m.p.  $154^\circ$  (126) (corresp. mono-(*p*-toluenesulfonate), m.p.  $151^\circ$  (127)); note that reaction of  $\bar{C}$  with 1 mole formaldehyde to give 4-chloro-2-(hydroxymethyl)phenol (5-chlorosalicyl alcohol) is not reported although the latter (Beil. VI-893), m.p.  $93^\circ$ , is known.]

With  $CHCl_3$ , chloral, or hexamethylenetetramine. [ $\bar{C}$  with  $CHCl_3 + EtOH + aq. NaOH$  (128), or  $\bar{C}$  with hexamethylenetetramine in anhydrous glyceroboric acid at  $150-155^\circ$  followed by  $H_2SO_4$  hydrolysis (129), or  $\bar{C}$  with chloral + anhydrous  $Na_2HPO_4$  at  $70-75^\circ$  (giving (4-chloro-2-hydroxyphenyl)-trichloromethyl-carbinol cf. (130)) followed by hydrolysis + oxidation (131), gives (18% yield (129)) 5-chloro-2-hydroxybenzaldehyde (5-chlorosalicylaldehyde) (3:2800), m.p.  $99-100^\circ$ .]

With  $\text{CCl}_4$ . [ $\bar{\text{C}}$  with  $\text{CCl}_4$  in aq.  $\text{NaOH}$  (128) in pres. of  $\text{Cu}$  or  $\text{Cu}$  compds. (132) or  $\bar{\text{C}}$  with  $\text{CCl}_4$  in alc.  $\text{KOH}$  in s.t. at  $140^\circ$  for 5-6 hrs. (133) gives 5-chloro-2-hydroxybenzoic acid (5-chlorosalicylic acid) (3:4705), m.p.  $172^\circ$ .]

With  $\text{CO}_2$  or organic acids. [ $\bar{\text{C}}$  (as dry  $\text{Na}\bar{\text{A}}$ ) with  $\text{CO}_2$  at  $140$ – $150^\circ$  under press. gives (135) (136) Na salt of 5-chlorosalicylic acid (3:4705) (see also above).]

[ $\bar{\text{C}}$  with *o*-chlorobenzoic acid (3:4150) in  $\text{MeOH}/\text{NaOMe}$  + trace  $\text{Cu}$  powder evapd., htd. at  $200^\circ$ , then htd. with conc.  $\text{H}_2\text{SO}_4$  for 15 min. gives (136) 2-chloroxanthone, m.p.  $165^\circ$  (136).]

With acid chlorides of organic acids. The conventional type of reaction of  $\bar{\text{C}}$  with acyl halides is to form the corresp. *p*-chlorophenyl esters (see also below under reactions of phenolic hydrogen of  $\bar{\text{C}}$ ); however, with  $\bar{\text{C}}$  acid chlorides in pres. of  $\text{AlCl}_3$  the ultimate product (undoubtedly formed by rearr. of an intermediate ester) is the ketone [e.g.,  $\bar{\text{C}}$  with benzoyl chloride (3:6240) +  $\text{AlCl}_3$  in  $\text{CS}_2$  (137) or acetylene tetrachloride (3:5750) (138) gives 4-chloro-2-benzoylphenol (5-chloro-2-hydroxybenzophenone), m.p.  $95.0$ – $95.5^\circ$  (138),  $94$ – $95^\circ$  (139),  $94^\circ$  (137),  $93$ – $94^\circ$  (140), frequently accompanied by *p*-chlorophenyl benzoate, m.p.  $87^\circ$  (see below); for analogous behavior of  $\bar{\text{C}}$  with *o*-toluyl chloride (3:8740) see (138)].

With anhydrides. [ $\bar{\text{C}}$  with phthalic anhydride (1:0725) +  $\text{AlCl}_3$  at  $140$ – $145^\circ$  (141) cf. (143) or in acetylene tetrachloride (3:5750) (142) gives (70% yield (142)) *o*-(5-chloro-2-hydroxybenzoyl)benzoic acid [Beil. X<sub>1</sub>-(470)], cryst. from hot  $\text{AcOH}$ , acetone, or alc., m.p.  $202^\circ$ , after sintering at  $102^\circ$  (142); this product ring-closes under the conditions of its formn. (141) (142) (143) (144) or with conc.  $\text{H}_2\text{SO}_4$  at  $100^\circ$  (144) (142) cf. (141) giving 4-chloro-1-hydroxyanthraquinone [Beil. VIII-340, VIII<sub>1</sub>-(651)], yel.-or. ndls. from  $\text{AcOH}$  or pyridine, m.p.  $194^\circ$  (141),  $103$ – $194^\circ$  (145),  $192$ – $103^\circ$  (146),  $189^\circ$  (142),  $188^\circ$  (147) (corresp. methyl ether, m.p.  $168^\circ$  (145), corresp. acetate, m.p.  $176$ – $177^\circ$  (146)), also ohtd. (70% yield (145)) directly from  $\bar{\text{C}}$  with phthalic anhydride (1:0725) +  $\text{AlCl}_3$  +  $\text{NaCl}$  at  $200$ – $220^\circ$  for 3 hrs. (See also next paragraph).]

[Note, however, that  $\bar{\text{C}}$  with phthalic anhydride (1:0725) + conc.  $\text{H}_2\text{SO}_4$  at  $200^\circ$  (148) (140) or in pres. of conc.  $\text{H}_2\text{SO}_4$  +  $\text{H}_3\text{BO}_3$  at  $200^\circ$  for  $3\frac{1}{2}$  hrs. (150) (151) (143) (152) (153) (154) (155) (156) goes further than above giving (yield: 68–74% (150)) 1,4-dihydroxyanthraquinone (quinizarin) (1:9085), cryst. from  $\text{AcOH}$ , m.p.  $200$ – $202^\circ$  cor. (150).]

[ $\bar{\text{C}}$  with 4-chlorophthalic anhydride (3:2725) +  $\text{H}_3\text{BO}_3$  + fume  $\text{H}_2\text{SO}_4$  at  $175$ – $195^\circ$  for 20 hrs. gives (167) 6-chloro-1,4-dihydroxyanthraquinone (6-chloroquinizarin), thls. from toluene, m.p.  $188^\circ$  (158) (corresp. dimethyl ether, m.p.  $168.5^\circ$  (158); diacetate, m.p.  $213^\circ$  (158)). — For completely analogous behavior under similar circumstances of  $\bar{\text{C}}$  with 3,4-dichlorophthalic anhydride (3:3695) or  $\bar{\text{C}}$  with 4,5-dichlorophthalic anhydride (3:4830) see these cpds.]

[ $\bar{\text{C}}$  with 4-sulfophthalic anhydride +  $\text{H}_3\text{BO}_3$  +  $\text{H}_2\text{SO}_4$  at  $200^\circ$  for 4 hrs. gives (45% yield (159) (160) cf. (161)) 1,4-dihydroxyanthraquinonesulfonic acid-6 (6-sulfoquinizarin) [Beil. XI-357]; for study of Na salt of latter as acid-base indicator see (162).]

[For behavior of  $\bar{\text{C}}$  with 3-methylphthalic anhydride +  $\text{AlCl}_3$  (144) (163), with 4-methylphthalic anhydride +  $\text{AlCl}_3$  (163), with naphthalene-1,2-dicarboxylic acid anhydride +  $\text{AlCl}_3$  +  $\text{NaCl}$  (164), or with naphthalene-2,3-dicarboxylic acid anhydride +  $\text{AlCl}_3$  +  $\text{NaCl}$  (165), see indic. refs.]

With esters of keto acids. [ $\bar{\text{C}}$  (1 mole) with ethyl acetoacetate (1:1710) + conc.  $\text{H}_2\text{SO}_4$  stood 24 hrs. gives (2.7% yield (166)) 6-chloro-2-methylcoumarin [Beil. XVII-336, XVII<sub>1</sub>-(173)], m.p.  $186$ – $187^\circ$  (167),  $186^\circ$  (168),  $185^\circ$  (170),  $184$ – $185^\circ$  (166),  $184^\circ$  (169); note, however, that 4-chloro-2-acetylphenol (5-chloro-2-hydroxyacetophenone) (see below) with  $\text{Ac}_2\text{O}$  +  $\text{NaOAc}$  at  $160$ – $170^\circ$  for 5 hrs. gives (167) both the above 6-chloro-2-methylcoumarin and the isomeric 6-chloro-2-methylchromone, ndls. from  $\text{AcOH}$ , m.p.  $115$ – $116^\circ$  (167).]

[Note also that  $\bar{\text{C}}$  with  $\alpha$ -alkylacetoacetates +  $\text{P}_2\text{O}_5$  gives the corresp. chromones: e.g.,

$\bar{C}$  with ethyl  $\alpha$ -methylacetoacetate (1:1712) gives (17% yield (171)) 6-chloro-2,3-dimethylchromone, m.p. 107°;  $\bar{C}$  with ethyl  $\alpha$ -ethylacetoacetate (1:1723) gives (171) 6-chloro-3-ethyl-2-methylchromone, m.p. 109°;  $\bar{C}$  with ethyl  $\alpha$ -(*n*-propyl)acetoacetate gives (172) 6-chloro-2-methyl-3-*n*-propylchromone, m.p. 108°;  $\bar{C}$  with ethyl  $\alpha$ -isopropylacetoacetate gives (172) 6-chloro-2-methyl-3-*n*-propylchromone, m.p. 108°;  $\bar{C}$  with ethyl  $\alpha$ -isopropylacetoacetate gives (172) 6-chloro-3-isopropyl-2-methylchromone, m.p. 127°.]

[ $\bar{C}$  with diethyl oxaloacetate + conc.  $H_2SO_4$  nt 0° gives (small yield (170)) ethyl 6-chlorocoumarin-4-carboxylate [Beil. XVIII<sub>1</sub>-(493)], yel. ndls., m.p. 96-97°;  $\bar{C}$  with diethyl acetonedicarboxylate (1:1772) + conc.  $H_2SO_4$  gives (6% yield (170)) ethyl 6-chlorocoumarinyl-4-acetate [Beil. XVIII<sub>1</sub>-(493)], m.p. 167°.]

With diazonium salts.  $\bar{C}$  in alk. soln. couples with diazonium salts giving upon acidification the corresp. chloro-hydroxy-azo derivs. [e.g.,  $\bar{C}$  with benzenediazonium chloride (aniline diazotized in HCl soln.) gives (173) 4-chloro-2-(benzeneazo)phenol (5-chloro-2-hydroxyazobenzene) [Beil. XVI-93], red-or. ndls. from AcOH, mp. 110-111° (173) (174);  $\bar{C}$  with diazotized *p*-nitroaniline gives (175) 4-chloro-2-(*p*-nitrobenzeneazo)phenol, m.p. 140-143°; for patent on coupling of  $\bar{C}$  with other diazonium salts see (176)].

With other miscellaneous reactants. [For condensation of  $\bar{C}$  with indene (di)chloride (2,3-dichloroindane) see (177); for condensation of  $\bar{C}$  with *o*-nitrobenzenesulfonic acid (178) or with 2-chloro-5-nitrobenzenesulfonic acid (179) see indic. refs.; for oxidative condensation of  $\bar{C}$  with *N,N*-dialkyl-*p*-phenylenediamines, etc., to give various indophenols see (180).]

[ $\bar{C}$  (2 moles) with  $SOCl_2$  (1 mole) in  $CCl_4$  at -10° (181) or in  $CS_2$  at 40-45° (70% yield (182)) or  $\bar{C}$  with  $S_2Cl_2$  in  $CS_2$  nt room temp. (42% yield (182)) gives bis-(5-chloro-2-hydroxyphenyl) sulfide [Beil. VI<sub>1</sub>-(396)], ndls. or lts. from  $C_6H_6$ , m.p. 175° (183), 174° (182), 173-174° (184), 173° (181) (corresp. dimethyl ether, m.p. 112° (182); diethyl ether, m.p. 145° (185), dibenzoate, m.p. 145° (182)); for use as disinfectant (181) (183) or in moth-proofing compositions (186) see indic. refs.]

[ $\bar{C}$  (2 moles) with  $SOCl_2$  (1 mole) +  $AlCl_3$  in  $CS_2$  gives (70% yield (184)) bis-(5-chloro-2-hydroxyphenyl) sulfoxide [Beil. VI<sub>1</sub>-(396)], pr. from dil. alc., m.p. 202° (corresp. dinitration prod., m.p. 180-181° (184)) ]

#### REACTIONS INVOLVING NUCLEAR HALOGEN OF $\bar{C}$

[ $\bar{C}$  on fusion with KOH (187) (188) or  $\bar{C}$  with aq. alkali or alk. carbonates in pres. of Cu or Cu compds. at elevated temp. under press. (189), or  $\bar{C}$  with aq.  $Ba(OH)_2$  nt 170-195° under press. (190), or  $\bar{C}$  with alkali or alk.-earth hydroxides + Cu salts at elevated temp. under press. (191) gives 1,4-dihydroxybenzene (hydroquinone) (1:1590); note, however, that in such fusions with alkali some 1,3-dihydroxybenzene (resorcinol) (1:1530) is also formed (187) (188) (192) (193), and  $\bar{C}$  (as Na $\bar{A}$ ) with NaOH at 310° for 5 hrs. gives (194) as high as 38% resorcinol (1:1530) + a trace of 2,4'-dihydroxybiphenyl; however,  $\bar{C}$  on fusion with  $K_2CO_3$  is claimed (193) to yield only hydroquinone (1:1590).]

[ $\bar{C}$  with  $Na_2S$  + NaOH nt 210-215° for 24 hrs. gives (195) 4-mercaptophenol (monothiohydroquinone) [Beil. VI-859, VI<sub>1</sub>-(410)], m.p. 29-30°]

[ $\bar{C}$  with  $NH_3$  in pres. of Cu cpds. htd. under press. gives (196) *p*-aminophenol;  $\bar{C}$  similarly with prim. aliphatic amines gives (196) corresp. *N*-alkyl-*p*-aminophenols.]

#### REACTIONS OF $\bar{C}$ INVOLVING PHENOLIC H (I.E., H OF THE OH GROUP)

Acidic strength.  $\bar{C}$  behaves as weak acid, is soluble in aq. alk. or in large excess (2.75 moles of 2 *N* (197)) aq.  $Na_2CO_3$  soln. from which it is reprecipitated by  $CO_2$  (197). — Dissoc. const. of  $\bar{C}$  in aq. at 28.5° =  $6.6 \times 10^{-10}$  (198); for studies of dissoc. const. in other solutions, e.g., in 50% MeOH at 20° (199) (200) or at 28.5° (198), or at 18° over range 0-95% MeOH by volume (203), in 30% aq. EtOH at 25° (200) (9) (201), or at 18° over range

0-95% EtOH by vol. (202), see indic. refs. — For hydrogen potential of  $\bar{C}$  in 48.95 vol. % EtOH or 95 vol. % EtOH at 20° see (204). — For titration of  $\bar{C}$  with standard NaOH and indicator see (205).

Salts of  $\bar{C}$ . (Na $\bar{A}$ ; from  $\bar{C}$  in nbs. EtOH with equiv. Na, evapd. under H<sub>2</sub>, dried at 140-150° (134); very hygroscopic ndls. from conc. alc. soln., turning brown in air; in contrast to Na phenolate is fairly eas. sol. dry ether (206); for behavior with CO<sub>2</sub> at 140-150° giving Na salt of 5-chlorosalicylic acid (3:4705) see (134) (135).]

[ $\bar{C}$  (38.4 pts.) with KOH (5.6 pts.) in C<sub>6</sub>H<sub>6</sub> gives (207) K $\bar{A}$ .2 $\bar{C}$ .]

[ $\bar{C}$  with AlCl<sub>3</sub> evolves heat and HCl giving (208) Cl.C<sub>6</sub>H<sub>4</sub>.OAlCl<sub>2</sub>, m.p. 185-187° (208).]

[For patents on use of alkali salts of  $\bar{C}$  as anti-gumming agents for motor fuels see (209); for use of aq. solns. of salts of  $\bar{C}$  as wash liquid for fuel gas purification see (210).]

#### ETHERIFICATION (see also below under $\bar{C}$ 's)

Aliphatic ethers of  $\bar{C}$ .  $\bar{C}$  with alkyl halides usually in presence of an acid acceptor gives the corresponding *p*-chlorophenyl ethers (e.g., for methyl ether (*p*-chloroanisole) (3:6300) or for ethyl ether (*p*-chlorophenetole) (3:0090) see these compds. — *p*-Chlorophenyl *n*-propyl ether appears to be unreported; for *p*-chlorophenyl isopropyl ether, h.p. 101° at 17 mm. (211), 73-75° nt 1.5 mm. (212),  $n_D^{25} = 1.5127$  (212), see indic. refs. — For *p*-chlorophenyl isobutyl ether, b.p. 95-97° at 3 mm.,  $n_D^{25} = 1.5090$ , see (213); the *n*-butyl, *sec*-butyl and *ter*-butyl ethers are unreported. — For *p*-chlorophenyl *n*-amyl ether, b.p. 132-133° at 12 mm., *p*-chlorophenyl *n*-heptyl ether, b.p. 172° at 34 mm., *p*-chlorophenyl *n*-heptyl ether, b.p. 162° at 14 mm., and *p*-chlorophenyl *n*-hexadecyl ether, m.p. 48°, see (214)].

[ $\bar{C}$  with vinyl chloride (3:7010) + aq. NaOH + CuCl<sub>2</sub> at 170-190° for 10 hrs. under press. gives (215) *p*-chlorophenyl vinyl ether, b.p. 193-194°,  $D_{20}^{20} = 1.138$ . —  $\bar{C}$  with allyl bromide + K<sub>2</sub>CO<sub>3</sub> in acetone gives (100% yield (216)) *p*-chlorophenyl allyl ether, h.p. 232-234° at ord. press., 106-107° at 12 mm.; note that distn. at ord. press. causes thermal rearr. to 4-chloro-2-allylphenol, b.p. 137° at 18 mm., 124-125° at 12 mm., m.p. 48° (corresp. *p*-nitrobenzoate, m.p. 82°) (216). —  $\bar{C}$  with methallyl chloride (3:7145) + K<sub>2</sub>CO<sub>3</sub> in acetone gives (217) *p*-chlorophenyl methylallyl ether, b.p. 101.5° at 8 mm.,  $D_{20}^{20} = 1.0979$ ,  $n_D^{20} = 1.5394$ ; this prod. on thermal rearr. gives (217) 4-chloro-2-methallylphenol, h.p. 113° at 8 mm.,  $D_{20}^{20} = 1.145$ ,  $n_D^{20} = 1.5622$ , accompanied by some 5-chloro-2,2-dimethylcoumaran, b.p. 96° at 5 mm.,  $D_{20}^{20} = 1.135$ ,  $n_D^{20} = 1.5300$  (217).]

[ $\bar{C}$  with ethylene oxide (1:6105) in alc. NaOEt adds giving (218) cf. (219) ethylene glycol mono-(*p*-chlorophenyl) ether (*p*-chlorophenyl  $\beta$ -hydroxyethyl ether), m.p. about 28° (corresp. *p*-nitrobenzoate, m.p. 90-91°) (218); note that the corresp. ethylene glycol bis-(*p*-chlorophenyl ether) is unreported.]

[ $\bar{C}$  (as Na $\bar{A}$ ) with 2-chloropropanol-1 (3:7917) gives (220) *p*-chlorophenyl  $\beta$ -hydroxyisopropyl ether (propylene glycol  $\beta$ -(*p*-chlorophenyl) ether), h.p. 151-153° at 18 mm. —  $\bar{C}$  with 3-chloropropanediol-1,2 (glycerol  $\alpha$ -monochlorohydrin) (3:9038) in alk. soln. (221), or  $\bar{C}$  with glycerol (1:6540) + NaOAc nt 200-210° in atmosphere of illuminating gas (222) gives *p*-chlorophenyl  $\beta,\gamma$ -dihydroxy-*n*-propyl ether (glycerol  $\alpha$ -(*p*-chlorophenyl) ether), cryst. from C<sub>6</sub>H<sub>6</sub>, m.p. 80° (221), 76° (222); b.p. 214-215° at 19 mm. (221), 173-175° at 17 mm. (223).]

[ $\bar{C}$  with diethyl chlorofumarate (3:6864) + NaOEt at 150° gives (224) diethyl *p*-chlorophenoxyfumarate, h.p. 199-200° at 12 mm. —  $\bar{C}$  (as Na $\bar{A}$ ) +  $\bar{C}$  with ethyl phenylpropiolate as directed gives (224) ethyl  $\beta$ -(*p*-chlorophenoxy)cinnamate, m.p. 63-64°, b.p. 220-225° at 12 mm.]

Aromatic ethers of  $\bar{C}$ . . . . . at 19 mm. (225), 146-150° at 7 mm. (226), . . . . . prod. has not been reported by etherification . . . . . (1:7125) in AcOH

with  $\text{Cl}_2$  (226), from K phenolate + *p*-chloriodobenzene (225), or from *p*-aminophenol phenyl ether via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reaction (226); for studies of its chlorination, bromination, iodination, and nitration see (226), for metalation see (227); note also that the product first reported (228) was impure (225).]

*p*-Chlorophenyl *p*-chlorophenyl ether (*bis*-(*p*-chlorophenyl) ether) [m.p.  $30^\circ$  (226) (229), b.p.  $168-172^\circ$  at 7 mm (226); note that this prod. has not been reported by etherification of  $\hat{\text{C}}$  but has been prepd. from diphenyl ether (1:7125) in AcOH with  $\text{Cl}_2$  (226), or from *p*-aminophenol *p*-chlorophenyl ether via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reaction (226) (229); for mononitration to 4-chlorophenyl 4-chloro-2-nitrophenyl ether, m.p.  $75^\circ$  (see also below) or dinitration to *bis*-(1-chloro-2-nitrophenyl) ether, m.p.  $152^\circ$  (229),  $154^\circ$  (230), see (229) (230)]

*p*-Chlorophenyl *o*-nitrophenyl ether [from  $\hat{\text{C}}$  (as  $\text{K}\hat{\text{A}}$ ) with *o*-chloronitrobenzene on htg (230) (231) in pres. of Cu bronze (232) (yields: 75% (232), 72% (230)), pale yel. cryst. from MeOH, m.p.  $46^\circ$  (231),  $45.5^\circ$  (230),  $44-45^\circ$  (232), b.p.  $220^\circ$  at 20 mm. (232),  $208^\circ$  at 11 mm. (232); note that this prod. does not (229) react with piperidine at  $100^\circ$ ]

*p*-Chlorophenyl *m*-nitrophenyl ether [m.p.  $60^\circ$  (233), reported only by indirect means (233)].  
*p*-Chlorophenyl *p*-nitrophenyl ether: from  $\hat{\text{C}}$  (as  $\text{K}\hat{\text{A}}$ ) with *p*-chloronitrobenzene on htg (81% yield (230)) (229) (233), m.p.  $76.5^\circ$  (230),  $76^\circ$  (233),  $75.5-76^\circ$  (229); b.p.  $215^\circ$  at 12 mm. (229) or as one prod. of nitration of *p*-chlorophenyl phenyl ether (above) (226) — [For pat. on use as insecticide see (131)]

*p*-Chlorophenyl 2,4-dinitrophenyl ether: from  $\hat{\text{C}}$  (as  $\text{K}\hat{\text{A}}$  (230) or  $\text{Na}\hat{\text{A}}$  (235)) with 2,4-dinitrochlorobenzene on htg (97% yield (230)); yel. tbls. from 1:2 EtOH/AcOH, m.p.  $126^\circ$  (235),  $123^\circ$  (230).

*p*-Chlorophenyl 2,4,6-trinitrophenyl ether [This prod. which should easily be obtd. from  $\hat{\text{C}}$  (as  $\text{K}\hat{\text{A}}$ ) with 2,4,6-trinitrochlorobenzene (picryl chloride) appears to be unreported.]

*p*-Chlorophenyl 4-chloro-2-nitrophenyl ether: from  $\hat{\text{C}}$  (as  $\text{K}\hat{\text{A}}$ ) with 2,5-dichloronitrobenzene on htg. (81.4% yield (230)) (229) (231) (81), pale yel. ndls. from alc., m.p.  $70^\circ$  (230),  $78^\circ$  (231),  $75^\circ$  (229); b.p.  $215-220^\circ$  at 15 mm (229)

*p*-Chlorophenyl 4-bromo-2-nitrophenyl ether: from  $\hat{\text{C}}$  (as  $\text{K}\hat{\text{A}}$ ) with 2,5-dibromonitrobenzene on htg. (91.0% yield (230)) (236), pale yel. ndls. from AcOH, m.p.  $100-101^\circ$  (236),  $100.5^\circ$  (230).

### ESTERIFICATION

Esters of inorganic acids. [ $\hat{\text{C}}$  with  $\text{SOCl}_2$  + pyridine in  $\text{C}_6\text{H}_6$  as directed gives (237) (238) *bis*-(*p*-chlorophenyl) sulfite, b.p.  $213-214^\circ$  at 12 mm., sl. dec.]

[ $\hat{\text{C}}$  (3 moles) with  $\text{PCl}_3$  (1 mole) at  $150^\circ$  gives (239) *tris*-(*p*-chlorophenyl) phosphite, m.p.  $49^\circ$ , b.p.  $290-297^\circ$  at 15 mm. (corresp. MeI addn. prod., m.p.  $71^\circ$  (239)), note, however, that  $\hat{\text{C}}$  with large excess  $\text{PCl}_3$  at  $100^\circ$  gives (210) *p*-chlorophenylphosphorous dichloride  $\text{Cl C}_6\text{H}_4\text{OPCl}_2$ , b.p.  $128-130^\circ$  at 12 mm., and di-(*p*-chlorophenyl)phosphorous chloride  $(\text{Cl C}_6\text{H}_4\text{O})_2\text{P}-\text{Cl}$ , b.p.  $225-227^\circ$  at 11 mm.]

[ $\hat{\text{C}}$  (3 moles) with  $\text{POCl}_3$  (1 mole) under reflux (211), or  $\hat{\text{C}}$  with  $\text{POCl}_3$  in cold alk. soln. (242) (213), or  $\hat{\text{C}}$  (as  $\text{Na}\hat{\text{A}}$ ) with  $\text{POCl}_3$  in neutral inert solv. (211), gives tri-(*p*-chlorophenyl) phosphate [Bd. VI-188, VI-(102)], m.p.  $117^\circ$  (211),  $112^\circ$  (211) — Note, however, that  $\hat{\text{C}}$  with  $\text{POCl}_3$  in pres. of Mg at  $130-140^\circ$  gives (215) *p*-chlorophenylphosphoryl dichloride,  $\text{Cl C}_6\text{H}_4\text{O}-\text{P}(\text{O})\text{Cl}_2$  [Bd. VI-188, VI-(102)], b.p.  $263^\circ$  at 760 mm. (216) (217),  $141^\circ$  at 12 mm. (216),  $95-115^\circ$  at 0.1 mm. (215), accompanied by di-(*p*-chlorophenyl)phosphoryl chloride  $(\text{Cl C}_6\text{H}_4\text{O})_2\text{P}(\text{O})\text{Cl}$  [Bd. VI-188], b.p.  $161-176^\circ$  at 0.1 mm. (215); these two products are highly hydrolyzed, respectively, to *p*-chlorophenylphosphonic acid [Bd. VI-188] cf. (218), m.p.  $80-81^\circ$  (219), and di-(*p*-chlorophenyl)phosphoric acid [Bd. VI-188], m.p.  $126-127^\circ$  (212),  $133-135^\circ$  cor. (218) (220).]

[For analogous behavior of  $\bar{C}$  with  $TiCl_4$  see (251).]

Esters of aliphatic organic acids (see also below under  $\textcircled{D}$ 's).

*p*-Chlorophenyl acetate: from  $\bar{C}$  with  $Ac_2O + NaOAc$  (252); m.p. 7–8° (252), h.p. 226–228° (253), 100–102° at 15 mm. (254), 108° at 12.5 mm. (252), 90–92° at 2.5 mm. (61),  $D_4^{20} = 1.2248$  (252). — Note that this prod. with  $AlCl_3$  on htg. (255) (254) (61) or  $\bar{C}$  with  $AcCl + FeCl_3$  directly (256) gives (100% yield (255)) 4-chloro-2-acetylphenol (5-chloro-2-hydroxyacetophenone) [Beil. VIII-86], m.p. 55° (256), 54° (61), 63.5–54.6° (167), b.p. 97–99° at 2 mm. (61) (corresp. acetate, b.p. 156–157° (140)).

*p*-Chlorophenyl propionate: from  $\bar{C}$  with propionyl chloride (3:7170) (140) (61); oil, h.p. 234–236° (140), 76–78° at 2 mm. (61). — Note that this prod. with  $AlCl_3$  undergoes Fries rearr. giving (140) (61) 4-chloro-2-propionylphenol (5-chloro-2-hydroxypropionophenone), m.p. 59.7° (61), 56.5–57.5° (140) (corresp. methyl ether, m.p. 41–42°, b.p. 135–140° at 6 mm. (257)).

*p*-Chlorophenyl *n*-butyrate: from  $\bar{C}$  with *n*-butyryl chloride (3:7370) (140) (61); oil, b.p. 249–251° (140), 96–98° at 3 mm. (61). — Note that this prod. with  $AlCl_3$  undergoes Fries rearr. giving (140) (61) 4-chloro-2-(*n*-butyryl)phenol (5-chloro-2-hydroxy-*n*-butyropenone), m.p. 50.5° (61), 49–50° (140); h.p. 108–112° at 3 mm. (61).

*p*-Chlorophenyl isobutyrate: from  $\bar{C}$  with isobutyric acid (1:1030) +  $POCl_3$  (258); m.p. 29°, b.p. 120° at 11 mm. (258). — Note that this prod. with  $AlCl_3$  undergoes Fries rearr. giving (258) 4-chloro-2-isobutyrylphenol (5-chloro-2-hydroxy-isobutyropenone), oil, h.p. 130° at 20 mm.,  $D_4^{20} = 1.192$ ,  $n_D^{20} = 1.5521$  (258).

[For generally analogous behavior of  $\bar{C}$  with *n*-valeryl chloride (3:7740), *n*-caproyl chloride (3:8168), *n*-heptanoyl chloride (3:8520), *n*-octanoyl chloride (3:8680) see (61); with chloroacetyl chloride (3:5235) see (259); with  $\alpha$ -bromo-isovaleryl bromide see (260).]

$\bar{C}$  (as  $Na\bar{A}$ ) (2 moles) with  $COCl_2$  (3:5000) in  $C_6H_6$  at 130–180° under press. (261) or  $\bar{C}$  (as  $K\bar{A}$ ) in conc. aq. soln. with  $COCl_2$  in toluene (262), or  $\bar{C}$  with trichloromethyl chloroformate (dipsogenc) (3:5515) + aq.  $NaOH$  (263), gives di-(*p*-chlorophenyl) carbonate [Beil. VI-187], m.p. 147° (263), 144–145° (264).

Esters of aromatic organic acids (see also below under  $\textcircled{D}$ 's).

*p*-Chlorophenyl benzoate: from  $\bar{C}$  with benzoyl chloride (3:6240) (265) (for study of rate at 25° see (268)) in pres. of aq.  $NaOH$  (252) (266) (267); m.p. 87–87.5° (138), 87° u.c. (252), 86° (266) (267) — Note that this prod. with  $AlCl_3$  undergoes Fries rearr. giving (140) 4-chloro-2-benzoylphenol (5-chloro-2-hydroxybenzophenone), m.p. 95.0–95.5° (138), 94–95° (139), 94° (137), 93–94° (140) (corresp. benzoate, m.p. 112° (139)).

*p*-Chlorophenyl cinnamate: from  $\bar{C}$  with cinnamoyl chloride (3:0330) (68% yield (260)), m.p. 105° (260) (269).

— *p*-Chlorophenyl methyl ether (*p*-chloroanisole): oil. (See 3:6300.)

— *p*-Chlorophenyl ethyl ether (*p*-chlorophenetole): m.p. 20–21°. (See 3:0090.)

— *p*-Chlorophenyl acetate: m.p. 7–8° (252). [For further details see above under esters of  $\bar{C}$  with aliphatic organic acids.]

① *p*-Chlorophenyl benzoate: m.p. 87.0–87.5° (138), 87° u.c. (252), 86° (266) (267) [From  $\bar{C}$  with benzoyl chloride in pres. of aq.  $NaOH$  (252) (266) (267) (see also above under esters of  $\bar{C}$  with aromatic organic acids).]

— *p*-Chlorophenyl *o*-nitrobenzoate: unreported.

② *p*-Chlorophenyl *m*-nitrobenzoate: m.p. 124.5° (252). [From  $\bar{C}$  with *m*-nitrobenzoyl chloride + aq.  $NaOH$  (252).]

③ *p*-Chlorophenyl *p*-nitrobenzoate: m.p. 171° (270).

④ *p*-Chlorophenyl 3,5-dinitrobenzoate: m.p. 186° (271).

— *p*-Chlorophenyl benzenesulfonate: unreported.

— *p*-Chlorophenyl *p*-toluenesulfonate: unreported.

⑥ *p*-Chlorophenyl benzyl ether: ndls. from alc., m.p. 71° (272), 70–71° (273). [Note, however, that  $\bar{C}$  with benzyl chloride (3:8535) +  $AlCl_3$  gives not only this prod. but also (273) cf. (274) some Fries rearr. prod., viz., 4-chloro-2-benzylphenol (5-chloro-2-hydroxydiphenylmethane), m.p. 48–49° (273), 48.5° (274) (corresp. benzoate, m.p. 54–55°, benzenesulfonate, m.p. 68–69°, *p*-toluenesulfonate, m.p. 75.0–75.5° (273)).]

⑦ *p*-Chlorophenyl *p*-nitrobenzyl ether: cryst. from alc., m.p. 101.3° (275). [From  $\bar{C}$  + *p*-nitrobenzyl chloride (m.p. 71°) (or *p*-nitrobenzyl bromide, m.p. 99°) in alc. NaOEt (275).]

⑧ *p*-Chlorophenyl 2,4-dinitrophenyl ether: yel. thls. from 1:2 EtOH/AcOH, m.p. 126° (235), 123° (230). [From  $\bar{C}$  (as  $K\bar{A}$  (230) or  $Na\bar{A}$  (235)) with 2,4-dinitrochlorobenzene (m.p. 51°) on htg. (97% yield (230))]

⑨ *p*-Chlorophenoxyacetic acid (3.4375): pr. from hot aq., m.p. 156.7–157.2° cor. (279), 155–156.5° u.c. (276), 155–156° (277), 154–155° (278). [From  $\bar{C}$  with chloroacetic acid in aq. alk (279) (276) (277) (278)]

— *p*-Chlorophenyl *N*-phenylcarbamate: cryst. from alc., m.p. 138° (280), 137–138° (263). [From  $\bar{C}$  (as  $Na\bar{A}$ ) with phenylisocyanide dichloride on htg. (280); note, however, prepn. from  $\bar{C}$  + phenyl isocyanate has not been reported.]

⑩ *p*-Chlorophenyl *N*-(*p*-bromophenyl)carbamate: white pl. from  $C_6H_6$ /EtOAc, m.p. 196–197° cor. (281). [From  $\bar{C}$  with *p*-bromobenzazide (281) in lgr. (281).]

⑪ *p*-Chlorophenyl *N*-(*p*-iodophenyl)carbamate: m.p. 214–215° (282). [From  $\bar{C}$  with *p*-iodobenzazide (282) in lgr. (282)]

⑫ *p*-Chlorophenyl *N*-(*m*-nitrophenyl)carbamate: white pl. from lgr., m.p. 136° u.c., 139° cor. (283). [From  $\bar{C}$  with *m*-nitrobenzazide (283) or *m*-nitrophenyl isocyanate (283) in lgr. (283)]

⑬ *p*-Chlorophenyl *N*-(*p*-nitrophenyl)carbamate: pale yel. rods from lgr., m.p. 106° cor. (284). [From  $\bar{C}$  with *p*-nitrobenzazide (284) in lgr. (284).]

⑭ *p*-Chlorophenyl *N*-(3,6-dinitrophenyl)carbamate: yel. pl. from  $C_6H_6$ /EtOAc, m.p. 197–198° (285). [From  $\bar{C}$  with 3,5-dinitrobenzazide (285) in lgr. (285).]

⑮ *p*-Chlorophenyl *N*-(3,5-dinitro-4-methylphenyl)carbamate: pale yel. pl. from lgr., m.p. 206–207° u.c., 212–213° cor. (286). [From  $\bar{C}$  with 3,5-dinitro-4-methylbenzazide (286) in lgr. (286)]

⑯ *p*-Chlorophenyl *N*-( $\alpha$ -naphthyl)carbamate: m.p. 165–166° (287). [From  $\bar{C}$  with  $\alpha$ -naphthyl isocyanate in lgr. (287).]

⑰ *p*-Chlorophenyl *N*-( $\beta$ -naphthyl)carbamate: pl. from lgr., m.p. 165–166° u.c., 169–170° cor. (288). [From  $\bar{C}$  with  $\beta$ -naphthyl isocyanate (288) in lgr. (288).]

⑱ *p*-Chlorophenyl *N,N*-diphenylcarbamate: m.p. 97° (289). [From  $\bar{C}$  with *N,N*-diphenylcarbamyl chloride (289)]

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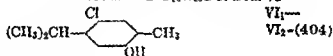
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**3:0480 4-CHLORO-5-ISOPROPYL-2-METHYLPHENOL**  $C_{10}H_{13}OCl$  *Beil. VI* —  
(*p*-(5)Chlorocarvacrol)



M.P. 42-43° (1) B.P. 158° at 52 mm. (2)  
138-140° at 12 mm. (3)  
135-136° at 12 mm. (1)

Volatile with steam.

[For prepn of  $\bar{C}$  from 2-hydroxy-*p*-cymene (carvacrol) (1,1760) with  $\text{Cl}_2$  (4) or with  $\text{SO}_2\text{Cl}_2$  (1) see indic. refs; from 4-chloro-5-isopropyl-2-methyl-aniline (5-chloro-2-amino-*p*-cymene) (2) via diazotization and subsequent hydrolysis see (2), from 5-amino-2-hydroxy-*p*-cymene (5-aminocarvacrol) via diazotization and subsequent reactn. with aq.  $\text{HCl}$  +  $\text{Cu}$  powder see (3); from 4-chloro-2-methylphenol (*p*-chloro-*o*-cresol) (3 0780) by reactn. with isopropyl alc. +  $\text{H}_2\text{SO}_4$  at 80° or in decalin soln. with propylene +  $\text{AlCl}_3$  see (5).]

[ $\bar{C}$  has outstanding bactericidal properties and is used ("Carvasept" (6)) as disinfectant, antiseptic, germicide, preservative (7), and anthelmintic (8) (9), for reviews of bactericidal actn. see (10) (11) (12) (13).]

[For solubilization of  $\bar{C}$  with soap solns. (14) and use of  $\bar{C}$  in soap solns. as disinfectant see (14) (15) (16); for prepn of esters of  $\bar{C}$ , e.g. the carbonate, m.p. 83-84° (from  $\bar{C}$  + dil. aq.  $\text{NaOH}$  + phosgene), or the saheylate, m.p. 60-61° (from  $\bar{C}$  + saheyllic acid +  $\text{POCl}_3$ ), see (17); for mercuration of  $\bar{C}$  see (18), for use of  $\bar{C}$  in mouth wash see (19).]

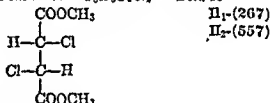
Ⓐ 4-Chloro-5-isopropyl-2-methylphenyl ethyl ether: m.p. 54-56° (17). [From  $\bar{C}$  in dil. aq.  $\text{NaOH}$  with  $\text{Et}_2\text{SO}_4$  (17)]

Ⓐ 4-Chloro-5-isopropyl-2-methylphenoxycetic acid: m.p. 160-161° (17). [From  $\bar{C}$  in dil. aq.  $\text{NaOH}$  with chloroacetic acid (17)]

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 4180 (1934). (18) Ghristianse  
 C.A. 35, 7657 (1941). (19) P  
 French 693,033, Nov. 14, 1930; *Cent.* 1931, I 1481.

- 3: 0485 DIMETHYL *d,l*- $\alpha,\alpha'$ -DICHLOROSUCCINATE  $C_6H_8O_4Cl_2$  Beil. II —  
 (Dimethyl *allo*-dichlorosuccinate;  
 dimethyl isodichlorosuccinate)

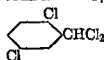


M.P. 43° (1) B.P. 116.5-120.5° cor. at 12.5 mm. (2)  
 42-43° (2) 105° at 3 mm. (1)

[For prepn. of  $\bar{C}$  from *d,l*- $\alpha,\alpha'$ -dichlorosuccinic acid (3:4711) in MeOH with  $H_2SO_4$  at  
 ord. temp. see (3); from dimethyl *d,l*-tartrate (1:2385) (1) or from dimethyl low-melting  
 $\beta$ -chloro-*d,l*-malate [Beil. III-438, III<sub>2</sub>-(290)] (2) with  $SOCl_2$  in pyridine see indic. refs.]  
 $\bar{C}$  with dimethylaniline loses 1 HCl yielding (1) dimethyl chlorofumarate (3:6582).

- 3: 0485 (1) Darzens, Séjourné, *Compt. rend.* 154, 1616 (1912). (2) Kuhn, Wagner-Jauregg,  
*Ber.* 61, 514 (1928). (3) Holmberg, *Arkiv. Kemi, Mineral. Geol.* 8, No. 2, 17, 33 (1920); *Cent.* 1921,  
 I 820; C.A. 19, 2116 (1922).

- 3: 0490 2,5-DICHLOROBENZAL (DI)CHLORIDE  $C_7H_4Cl_4$  Beil. V - 302  
 VI—  
 V<sub>2</sub>-(234)



M.P. 43° (1) B.P. 118-120° at 14 mm. (1)  
 42° (2) (3)

Cryst. from  $CHCl_3$ ; very eas. sol. org. solvents but spar. sol. in aq. —  $\bar{C}$  has faint but  
 not disagreeable odor. — Volatile with steam.

[For prepn. of  $\bar{C}$  from 2,5-dichlorobenzaldehyde (3:1145) with  $PCl_5$  (78% yield (1))  
 or with  $ClSO_3H$  in  $CHCl_3$  (3) see indic. refs.; from 2,5-dichlorotoluene (3:6245) at h.p.  
 with  $Cl_2$  see (2).]

$\bar{C}$  on hydrolysis, e.g., by protracted refluxing (56 hrs.) with aq. +  $CaCO_3$  (2), or by treat-  
 ment with fuming  $H_2SO_4$  (3), yields 2,5-dichlorobenzaldehyde (3:1145). [For study of  
 rate of hydrolysis in 50% alc. at 83.5° see (1).]

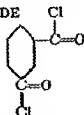
- 3: 0490 (1) Asinger, Lock, *Monatsh.* 62, 336-337 (1933). (2) de Crauw, *Rec. trav. chim.* 50, 773  
 (1931). (3) Gnehm, Schüle, *Ann.* 299, 359-360 (1898).

# CHAPTER III

## DIVISION A. SOLIDS

(3:0500-3:0999)

3:0520 ISOPHTHALYL (DI)CHLORIDE  
(isophthaloyl dichloride)



$C_8H_4O_2Cl_2$

Beil. IX - 834  
IX<sub>1</sub>-(372)

M.P.	B.P.			
43-44° (1)	276°	(3)	$D_4^{25} = 1.3872$ (9)	
42-43° (2)	200° (?)	at 15 mm. (7)		$n_D^{25} = 1.56999$ (9)
41-43° (18)	156°	at 15 mm. (8)		
41° (3) (4)	142.6-143°	at 14 mm. (5)		
40.5-41° (5)	143-144°	at 13 mm. (2)		
40° (6)	136°	at 11 mm. (18)		

Prisms from pet. ether.

[For prepn. of  $\bar{C}$  from isophthalic acid (1.0900) with  $PCl_5$  (3) in a s.t. at 200° (10) or in  $POCl_3$  (8) see indic. refs.; with  $AcCl$  (3-7065) in s.t. at 130° for 8 hrs. see (1); with  $SOCl_2$  (yield: 100% (6), 92% (18), 67% (2), 62% (7)) (5) see indic. refs.; for prepn. of  $\bar{C}$  from 1,3-bis-(trichloromethyl)benzene by partial catalytic hydrolysis see (4) (17).]

$\bar{C}$  with excess  $MeOH$  yields (11) dimethyl isophthalate (1:2214), m p. 67-68°; cf. also under isophthalic acid (1.0900);  $\bar{C}$  with excess phenol yields (3) diphenyl isophthalate, m p. 120° (3)

[ $\bar{C}$  on cat. hydrogenation in xylene with  $Pd$  cat. as specified (12) gives 83% yield isophthalaldehyde (Beil. VII-675, VII<sub>1</sub>-(361)), cryst. from alc., m p. 88-89° (12) (dioxime, m p. 178°; bis-phenylhydrazone, m p. 212-214° (12))]

[ $\bar{C}$  with  $AlCl_3$  + benzene yields (13) 1,3-dibenzoylbenzene (isophthalophenone) (Beil. VII-829, VII<sub>1</sub>-(443)), m p. 100-101° (dioxime, m p. 70-75° (10)); for corresp. reactn. of  $\bar{C}$  with *m*-xylene (1.7420) see (14); for corresp. reactn. of  $\bar{C}$  with anisole (1.7445) see (15)]

[For reactns. of  $\bar{C}$  with ethyl sodio-acetoacetate see (8) and with ethyl sodio-cyanoacetate see (16)] [For behavior of  $\bar{C}$  with diazomethane see (18).]

$\bar{C}$  on hydrolysis yields isophthalic acid (1:0900) q.v. for further characterization.

3:0520 (1) Liebermann, Kardos, *Ber.* 46, 211 (1913). (2) Reindel, Siegel, *Ber.* 56, 1554 (1923). (3) Schroder, *Ber.* 7, 708 (1874). (4) I G. French 820,697, Nov. 16, 1937, *Cent.* 1038, 1 1601; *C.A.* 32, 3422 (1935). (5) Koldrausch, Pongratz, Stockmair, *Monatsh.* 67, 109 (1935). (6) Meyer, *Monatsh.* 22, 436 (1901). (7) McMaster, Ahmann, *J. Am. Chem. Soc.* 50, 145 (1928). (8) Ruggli, Gassenmeier, *Helv. Chim. Acta* 22, 499-500 (1939). (9) von Auwers, Schmidt, *Ber.* 45, 454 (1913). (10) Mûnchmeyer, *Ber.* 19, 1818-1819 (1886).

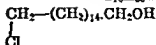
(11) Breyer, Villiger, *Ann.* 276, 258 (1931). (12) Roenmund, *Zetsche, Ber.* 54, 2890 (1921). (13) Ador, *Ber.* 13, 320 (1880). (14) Clar, John, Hawran, *Ber.* 62, 915 (1929). (15) Weiss, Chledowski, *Monatsh.* 65, 358, 362-363 (1935). (16) Sacher, *Bull. soc. chim.* (3) 11, 1097 (1894). (17) I G., Ger. 708,149, June 5, 1911; *C.A.* 37, 2746 (1913). (18) Ruggli, Knecht, *Helv. chim. Acta* 27, 1108-1115 (1914); *C.A.* 39, 4557 (1915).

## 3:0525 16-CHLOROHEXADECANOL-1

 $C_{16}H_{33}OCl$ 

Beil. S.N. 24

( $\omega$ -Chloro-*n*-hexadecyl alcohol;  
 $\omega$ -Chloropalmityl alcohol)



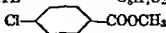
M.P. 43° (1)

Colorless cryst. from lt. pet.

[For prepn. of  $\bar{C}$  from  $\alpha, \omega$ -hexadecamethylene glycol [Beil. I<sub>2</sub>-(565)] (m.p. 87-88° (1)) with  $\text{SOCl}_2$  + dimethylaniline in  $\text{C}_6\text{H}_6$  (60% yield) see (1); note that a little 1,16-dichlorohexadecane, cryst. from MeOH, m.p. 47°, is also formed.]

3:0525 (1) Bennett, Gudgeon, *J. Chem. Soc.* 1933, 1679-1681.3:0535 METHYL *p*-CHLOROBENZOATE $\text{C}_8\text{H}_7\text{O}_2\text{Cl}$ 

Beil. IX - 340

IX<sub>1</sub>-

M.P. 44° (1)

43-43.5° (2) (6)

43° (3) (4)

42° (5)

34° (9)

[For prepn. of  $\bar{C}$  from *p*-chlorobenzoic acid (3:4940) with MeOH + HCl (2) or MeOH +  $\text{H}_2\text{SO}_4$  (2) (6) see indic. refs.; from  $\text{Ag}\bar{A}$  + MeI in s.t. at 100° see (5); from *p*-chlorobenzoyl chloride (3:6350) with MeOH see (3).]

$\bar{C}$  on htg. with sirupy  $\text{H}_3\text{PO}_4$  at 200° yields (7) *p*-chlorobenzoic acid (3:4940), dimethyl ether, and probably some *p*-chlorotoluene (3:8287).

$\bar{C}$  added to 5-6 pts. very conc.  $\text{HNO}_3$  at 0°, poured onto ice, yields (3) methyl 4-chloro-3-nitrobenzoate [Beil. IX-402], cryst. from MeOH, m.p. 83° (3).

[ $\bar{C}$  with Na + methyl acetate condenses giving (60% yield (6)) methyl *p*-chlorobenzoyl-acetate, b.p. 172° at 12 mm., m.p. 36-37° (6); this prod. with excess phenylhydrazine in alc. + AcOH gives on htg. 3-(*p*-chlorophenyl)-1-phenylpyrazolone-5, or. cryst. from AcOH, m.p. 140° (6); corresp. prod. from *p*-nitrophenylhydrazine, m.p. 200-205° (6).]

$\bar{C}$  on hydrolysis (Sap. Eq. = 170.5) yields methyl alcohol (1:6120) + *p*-chlorobenzoic acid (3:4940). [For studies of hydrolysis under various cond. see (2) (4).] — For the amide, anilide, *p*-toluidide, and other deriva. corresp. to  $\bar{C}$  see *p*-chlorobenzoic acid (3:4940).

3:0535 (1) Jaeger, *Z. Krist.* 42, 22 (1907). (2) Kellas, *Z. physik. Chem.* 24, 243-252 (1897). (3) Montagne, *Rec. trav. chim.* 19, 55-56, 61-64 (1900). (4) Jones, McCombie, Scarborough, *J. Chem. Soc.* 123, 2694-2697 (1923). (5) Emmerling, *Ber.* 8, 883 (1875). (6) Wahl, Rolland, *Ann. chim.* (10) 10, 9-12, 15-17 (1928). (7) Raikow, Tschkow, *Chem. Ztg.* 29, 1269 (1905). (8) Berger, *Rec. trav. chim.* 43, 170 (1924). (9) Kahovec, Wagner, *Monatsh.* 74, 285 (1943).

## 3:0550 3,4-DICHLOROBENZALDEHYDE

 $\text{C}_7\text{H}_4\text{OCl}_2$ 

Beil. VII - 238

VII<sub>1</sub>-(134)

M.P. 44° (1) B.P. 247-248° (2)

43-44° (2)

42.0-42.6° (3)

Colorless ndls. from alc. (1), odor like benzaldehyde (2). — Eas. volatile with steam (2) (3).

[For prepn. of  $\bar{C}$  from 3,4-dichlorotoluene (3:6355) via chlorination to 3,4-dichlorobenzal

(di)chloride (3:6876) and hydrolysis of the latter with fuming  $\text{H}_2\text{SO}_4$  (5%  $\text{SO}_2$ ) (36% yield (3)), conc.  $\text{H}_2\text{SO}_4$  (4), or  $\text{CaCO}_3 + \text{H}_2\text{O}$  (40% yield (3)) see (2) (3) (4); for prepn. from 4-chloro-3-nitrobenzaldehyde via reduction, diazotization, etc., see (1).]

$\bar{\text{C}}$  with satd. aq.  $\text{NaHSO}_3$  yields a cpd  $\bar{\text{C}}\text{NaHSO}_3$  (3). [Use in purification of  $\bar{\text{C}}$  (3).]  
 $\bar{\text{C}}$  on oxdn. with  $\text{KMnO}_4$  yields (2) 3,4-dichlorobenzoic acid (3:4925), m.p. 201–202° (3).  
 —  $\bar{\text{C}}$  with conc. aq.  $\text{KOH}$  undergoes Cannizzaro reactn. yielding 3,4-dichlorobenzyl alcohol, ndls. from aq., m.p. 38° (3), and 3,4-dichlorobenzoic acid (see above).

$\bar{\text{C}}$  on nitration as specified (5) (4) gives (71% yield (4)) 3,4-dichloro-6-nitrobenzaldehyde [Beil. VII-1(144)], yel. pr. from  $\text{C}_6\text{H}_6$ , m.p. 73° (5). [This product with  $\text{NH}_4\text{OH}/\text{AgNO}_3$  is oxidized (4) to 3,4-dichloro-6-nitrobenzoic acid, cryst. from  $\text{C}_6\text{H}_6$ , m.p. 165° (6).]

[For conversion of  $\bar{\text{C}}$  to 3,4-dichlorostyrene (7) (8) cf. (9) via reaction with  $\text{MeMgI}$  giving (73% yield (7)) 3,4-dichlorophenyl-methyl-carbinol (7) (8) and dehydration of latter with  $\text{KHSO}_4$  (yields 83% (8), 64% (7)) see indic. refs.]

Ⓒ 3,4-Dichlorobenzaldoxime (*anti* form): m.p. 114–115° (2), 118–119° (1). [The *syn* isomer, ndls. from alc., m.p. 120° rap. htg., is converted by fusion (2) to the *anti* form.]

— 3,4-Dichlorobenzaldehyde phenylhydrazone: unrecorded.

Ⓓ 3,4-Dichlorobenzaldehyde *p*-nitrophenylhydrazone: or. ndls., m.p. 276–277° (1).

— 3,4-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.

— 3,4-Dichlorobenzaldehyde semicarbazone: unrecorded.

3:0550 (1) Hodgson, Beard, *J. Chem. Soc.* 1927, 25. (2) Erdmann, Schwechten, *Ann.* 260, 72–73 (1890). (3) Krasny, *Rec. trav. chim.* 49, 1086 (1930). (4) Ruggli, Zaeslin, Lang, *Helv. Chim. Acta* 21, 1243 (1938). (5) Hoechst Farbwerke, Ger. 254,467, Dec. 3, 1912; *Cent.* 1913, I 199. (6) Ruggli, Zaeslin, *Helv. Chim. Acta* 19, 437 (1936). (7) Marvel, Overberger, Allen, Johnston, Saunders, Young, *J. Am. Chem. Soc.* 68, 863–864 (1946). (8) Brooks, *J. Am. Chem. Soc.* 66, 1295–1297 (1944). (9) Michalek, Clark, *Chem. & Eng. News* 22, 1539–1563 (1944).

### 3:0560 2,4-DICHLOROPHENOL


 $\text{C}_6\text{H}_4\text{OCl}_2$ 

Beil. VI - 189

VI-1(103)

VI-1(178)

M.P.		B.P.		
45°	(1) (2)	210.2–211.5° u.c.	(18)	$D_{25}^{25} = 1.4723$ (8)
43–44°	(17)	209–211°	(6) (11)	$n_D^{25} = 1.1729$ (8)
43°	(3) (4)	209–210°	(4)	
	(16) (18)	206–208° u.c. at 763 mm.	(7)	
42°	(5)	106.2–107.6° at 14–16 mm.	(3)	
41–42°	(11)			

Colorless ndls. from  $\text{C}_6\text{H}_6$ . —  $\bar{\text{C}}$  has unpleasant and persistent odor suggesting iodoform (1) (for study of strength of odor of aq. solns. of  $\bar{\text{C}}$  see (1)). —  $\bar{\text{C}}$  is spar. sol. aq. (100 g. aq. at 20° dis. 0.45 g.  $\bar{\text{C}}$ ), but is eas. sol. alc. ether,  $\text{C}_6\text{H}_6$ , or  $\text{CHCl}_3$ . —  $\bar{\text{C}}$  is volatile with steam; note, however, that from alk. soln.  $\bar{\text{C}}$  is not volatile with steam (dif. and sepn. from 2-chlorophenol (3:5980) or 4-chlorophenol (3:0475) (9)), although  $\bar{\text{C}}$  is volatile with steam from aq. solns. contg.  $\text{PbCO}_3$  (dif. and sepn. of  $\bar{\text{C}}$  from 2,4,6-trichlorophenol (3:1673) (9)). — Note that comm.  $\bar{\text{C}}$  often contains 2,4,6-trichlorophenol, and that  $\bar{\text{C}}$  prepd. by chlorination of phenol may cont. 2,6-dichlorophenol (3:1593).

[For prepn. of  $\bar{\text{C}}$  from *p*-chlorophenol (3:0475) or *o*-chlorophenol (3:5980) with  $\text{Cl}_2$  (1 mole) in  $\text{AcOH}$  soln. (80% yield) see (6); from phenol (1:1420) with  $\text{Cl}_2$  (2 moles) diluted with  $\text{CO}_2$  in  $\text{AcOH}$  and under these cond. giving exclusively  $\bar{\text{C}}$  see (7).]



[For formn. of  $\bar{C}$  (together with other prods.) from phenol (1:1420) with  $Cl_2$  (2 moles) (2) (1) (4) (10), with  $Cl_2$  (2 moles) in alk. soln. (11) (12), with *N,N'*-dichlorourea in HCl soln. (13), or with  $SO_2Cl_2$  (14) see indie. refs.; for formn. of  $\bar{C}$  from salicylic acid (1:0780) in excess aq. KOH with  $Cl_2$  see (15); from 3,5-dichloro-2-hydroxybenzoic acid (3,5-dichlorosalicylic acid) (3:4935) on distn. with lime see (16) (17); from 2,6-dichloro-3-hydroxybenzaldehyde (3:4160) in excess 50% aq. KOH on htg. at  $80^\circ$  (94% yield) see (5).]

Nuclear substitution of  $\bar{C}$ .  $\bar{C}$  in AcOH with  $Br_2$  (1 mole) (7) (18), or in 50% AcOH with  $Br_2$  (1 mole) in AcOH (19), yields 6-bromo-2,4-dichlorophenol, ndls. from  $C_6H_6$  or lt. pet., m.p.  $68-69^\circ$  (19),  $68^\circ$  (7) (18), h.p.  $268^\circ$  dec. (18),  $204^\circ$  at 19 mm. (19),  $198^\circ$  at 15 mm. (19),  $192^\circ$  at 12 mm. (19) (corresp. methyl ether, m.p.  $65^\circ$  (7); corresp. 2,4-dinitrophenyl ether, yel. lfts. from alc., m.p.  $140-141^\circ$  (19); corresp. *p*-toluenesulfonate, m.p.  $82-83^\circ$  (19)). — [This 6-bromo-2,4-dichlorophenol with excess  $Br_2$  in pres. of Fe powder and absence of aq. yields (20) 2,4-dichloro-3,5,6-tribromophenol, cryst. from AcOH, m.p.  $209^\circ$  (20) (corresp. methyl ether, m.p.  $143-144^\circ$  (20), corresp. benzoate, m.p.  $202^\circ$  (20)).]

$\bar{C}$  in aq. NaOH with  $I_2$  (1 mole) in aq. KI yields (7) 2,4-dichloro-6-iodophenol, ndls. from dil. alc., m.p.  $63^\circ$  (7) (corresp. methyl ether, m.p.  $35^\circ$ , h.p.  $278-285^\circ$  u.c. (7)).

$\bar{C}$  on nitration by soln. in cold fuming  $HNO_3$ , subsequently poured into aq. (4) cf. (21), yields 2,4-dichloro-6-nitrophenol [Beil. VI-241, VI-(122)], yel. cryst. from alc., m.p.  $121-122^\circ$  (4),  $124^\circ$  (22).

Condensation reactions involving nuclear hydrogens. [ $\bar{C}$  with formalin (1:0145) + conc. HCl + conc.  $H_2SO_4$  in pres. of stream of HCl gas at  $35-40^\circ$  (23), or  $\bar{C}$  with trioxymethylene + AcOH/ $H_2SO_4$  at  $50^\circ$  (24), gives (54% yield (23)) 6,8-dichlorobenzodioxane-1,3, volatile with steam, cryst. from MeOH, m.p.  $111^\circ$  (24),  $109-109.5^\circ$  (23). —  $\bar{C}$  with formalin (1:0145) + conc. HCl in stream of HCl gas at  $50^\circ$  for 36 hrs. gives (72% yield (23)) 3,5-dichloro-2-hydroxybenzyl chloride, ndls. from pet. eth., m.p.  $82-84^\circ$  (23); this prod. on hydrol. with aq. at  $50^\circ$  yields (23) 3,5-dichloro-2-hydroxybenzyl alc., ndls. from aq., m.p.  $80-81^\circ$ , also formed as hy-product of the dichlorobenzodioxane mentioned above.]

[ $\bar{C}$  with methylal (1:0105), methylene diacetate, or methylene (di)iodide in pres. of conc.  $H_2SO_4$  or  $ZnCl_2$  (25) or  $\bar{C}$  + formalin (1:0145) with AcOH/ $H_2SO_4$  (26) yields methylene-*bis*-(2,4-dichlorophenol) (2,2'-dihydroxy-3,5,3',5'-tetrachlorodiphenylmethane); for use of this prod. as mothproofing cpd., antiseptic, and seed disinfectant see (25) (26) (27) (28) (29) (30). — Note, however, that  $\bar{C}$  (as Na salt) with methylene (di)chloride (3:5020) at  $120-140^\circ$  in s.t. for 6 hrs. gives (24) *bis*-(2,4-dichlorophenoxy)methane, m.p.  $98^\circ$ . —  $\bar{C}$  with  $SCl_2$  or  $S_2Cl_2$  +  $AlCl_3$  in  $CS_2$  or  $CCl_4$  yields (31) 2,2'-dihydroxy-3,5,3',5'-tetrachlorodiphenyl sulfide, m.p.  $188^\circ$ . — For condens. of  $\bar{C}$  with benzaldehyde *o*- (or *p*-) sulfonic acids and use of products as mothproofing agts. see e.g. (26).]

[ $\bar{C}$  with phthalic anhydride (1:0725) +  $AlCl_3$  at  $150^\circ$  for 2 hrs. yields (36) cf. (37) (38) 2-(3',5'-dichloro-2'-hydroxybenzoyl)benzoic acid, colorless lfts. from alc., m.p.  $204^\circ$  cor. (36), which with conc.  $H_2SO_4$  ring-closes to 2,4-dichloro-1-hydroxyanthraquinone, yel. ndls. from  $C_6H_6$ , m.p.  $242^\circ$  (36),  $241-242^\circ$  (39). —  $\bar{C}$  with 4,5-dichlorophthalic anhydride (3:4830) + fuming  $H_2SO_4$  +  $H_3BO_3$  at  $195^\circ$  yields (40) 2,6,7-trichloro-1,4-dihydroxyanthraquinone (2,6,7-trichloroquinizarin).]

Reactions of the phenolic group of  $\bar{C}$  (see also under  $\bar{D}$  below).  $\bar{C}$  behaves as a weak acid:  $\bar{C}$  is sol. in aq. alk. but largely pptd. by  $CO_2$ . — Dissoc. const. at  $25^\circ$  in aq. is  $31. \times 10^{-7}$  (41) cf. (42).

[For study of bactericidal prop. of  $\bar{C}$  see (43); for use as insecticide in paper see (44); for prepn. and use of metal complexes as antiseptics see (45).]

[ $\bar{C}$  with alkali metals gives corresp. alk. 2,4-dichlorophenolates: K 2,4-dichlorophenolate with  $CO_2$  at  $140^\circ$  yields (15) 3,5-dichloro-2-hydroxybenzoic acid (3,5-dichlorosalicylic acid) (3:4935).]

[ $\bar{C}$  with ethyl  $\alpha$ -methylacetoacetate (1:1712) +  $P_2O_5$  gives (14.5% yield (46)) 6,8-dichloro-2,3-dimethylchromone (Beil. XVII-1-177)], ndls. from alc., m p. 141°.]

[ $\bar{C}$  in 20% aq. KOH htd. 2 hrs. at 100° with  $Me_2SO_4$  (22) cf. (1) yields 2,4-dichlorophenyl methyl ether (2,4-dichloroanisole) [Beil. VI-189, VI-1-103]], b.p. 232-233° cor. at 743.5 mm.; m.p. 27-28° (47). —  $\bar{C}$  with  $EtI$  +  $K_2CO_3$  in acetone refluxed 6-8 hrs. gives (90% yield (48)) 2,4-dichlorophenyl ethyl ether (2,4-dichlorophenetole), oil, b.p. 235-236° (48), 236-237° (4) (for study of cleavage of this ether with  $HBr/AcOH$  see (48), for study of rate of formation see (49)). —  $\bar{C}$  with allyl bromide +  $K_2CO_3$  in acetone yields (50) allyl 2,4-dichlorophenyl ether, b.p. 144-145° at 25 mm. (50).]

— 2,4-Dichlorophenyl acetate: oil, b.p. 241-245° (4), 167-168° at 80 mm. (51). [From  $\bar{C}$  with  $AcCl$  refluxed 40 min. (86% yield (51)), this ester with  $AlCl_3$  at 170° for 40 min. undergoes Fries rearr. giving (75% yield (51)) 3,5-dichloro-2-hydroxyacetophenone, m.p. 95-96° (51).]

⑤ 2,4-Dichlorophenyl benzoate: cryst. from alc., m.p. 96.5° (5), 96° (1), 97° [Beil. IX-117]. [From  $\bar{C}$  in dil. aq. NaOH shaken with  $BzCl$  (5) cf. (1)] [For study of nitration of this ester see (6).]

⑥ 2,4-Dichlorophenyl *m*-nitrobenzoate: ndls. from alc., m.p. 115-116° (6). [From  $\bar{C}$  + *m*-nitrobenzoyl chloride in dil. aq. alk.; for study of its nitration see (6).]

— 2,4-Dichlorophenyl *p*-nitrobenzoate: unreported.

— 2,4-Dichlorophenyl 3,6-dinitrobenzoate: unreported.

— 2,4-Dichlorophenyl benzenesulfonate: unreported.

\* ⑦ 2,4-Dichlorophenyl *p*-toluenesulfonate: pr. from alc., m.p. 125° (6).

⑧ 2,4-Dichlorophenyl benzyl ether: pr. from alc., ether, or pet. eth., m.p. 62° (52), 61-62° (53), 60° (54), 59.0-59.5° (55). [From  $\bar{C}$  + benzyl chloride (3:8335) +  $NaOEt$  in hot alc. (53), or from Na salt of  $\bar{C}$  + benzyl chloride in  $MeOH$  (55); note, however, that Na salt of  $\bar{C}$  with benzyl chloride in toluene at 160° for 5 hrs. undergoes instead nuclear alkylation yielding (55) 2,4-dichloro-6-benzylphenol (3,5-dichloro-2-hydroxydiphenylmethane), cryst. from pet. eth., m.p. 77.0-77.5° (55).]

⑨ 2,4-Dichlorophenyl *p*-nitrobenzyl ether: ndls. from ether, m.p. 148-150° (53).

⑩ 2,4-Dichlorophenyl 2,4-dinitrophenyl ether: lfts. from  $AcOH$ ,  $AcOH/EtOH$ , or  $EtOH$ , m.p. 119° (56), 118-119° (6), 118° (57). [From Na or K salt of  $\bar{C}$  + 2,4-dinitrochlorobenzene refluxed in alc. (56) (6) (57).]

⑪ 2,4-Dichlorophenoxyacetic acid (3:4095): cryst. from  $C_6H_6$ , m.p. 138° (58), Neut. Eq. = 221.0. [From  $\bar{C}$  + chloroacetic acid in slight excess aq. NaOH, refluxed and then acidified (87% yield (58)); for studies on use of this prod. as plant hormone see (59).]

— 2,4-Dichlorophenyl *N*-phenylcarbamate: unreported.

⑫ 2,4-Dichlorophenyl *N*-(*p*-iodophenyl)carbamate: m.p. 182-183° (61). [From  $\bar{C}$  + *p*-iodobenzazide in hot lgr (61).]

⑬ 2,4-Dichlorophenyl *N*-(*p*-bromophenyl)carbamate: rods from lgr/ $AcOEt$ , m.p. 169° cor. (62) [From  $\bar{C}$  + *p*-bromobenzazide in hot lgr. (62).]

⑭ 2,4-Dichlorophenyl *N*-(*p*-nitrophenyl)carbamate: yel. pl. from lgr./ $EtOAc$ , m.p. 205° cor. (62). [From  $\bar{C}$  + *p*-nitrobenzazide in hot lgr. (63).]

⑮ 2,4-Dichlorophenyl *N*-(3,5-dinitro-4-methylphenyl)carbamate: or.-yel. pr. from lgr. or  $EtOAc$ , m.p. 153° u.c., 157° cor. (64). [From  $\bar{C}$  + 3,5-dinitro-4-methylbenzazide in hot lgr (64).]

— 2,4-Dichlorophenyl *N*-( $\alpha$ -naphthyl)carbamate: unreported.

⑯ 2,4-Dichlorophenyl *N*-( $\beta$ -naphthyl)carbamate: pl. from lgr., m.p. 162° u.c., 166° cor. (65). [From  $\bar{C}$  +  $\beta$ -naphthyl isocyanate (or azide) in hot lgr. (65).]

similarly. —  $\bar{C}$  (1 mole) with salicylic acid (I:0780) in pyridine at  $-15^{\circ}$  (52) or in  $C_6H_6$  with dimethylaniline (63% yield (52)) gives *O*-carbethoxysalicylic acid [Beil. X-69, XI-(30)], m.p.  $95^{\circ}$  (other mono-, di-, and polyhydroxy phenolic acids behave similarly); since the carbethoxy groups so introduced may subsequently be removed by hydrolysis, this process has great value as a means of temporary blocking of phenolic groups (for further discussion and many references see (53)).]

[ $\bar{C}$  also reacts with the sodio derivatives and other metallic enolates: e.g.,  $\bar{C}$  (1 mole) with ethyl cyanoacetate (2 moles) in abs. alc. + NaOEt (2 moles) gives (54) diethyl cyanomalonate [Beil. II-S11, II<sub>1</sub>-(321), II<sub>2</sub>-(680)], b.p.  $135-140^{\circ}$  at 14 mm.,  $D_4^{20} = 1.128$ ,  $n_D^{20} = 1.4295$  (55). —  $\bar{C}$  with diethyl malonate (I:3581) + NaOEt in alc. (56) or  $\bar{C}$  with dry diethyl sodio-malonate (57) directly (58) (59) or in  $C_6H_6$  refluxed for 10 hrs. (60) gives (yields: 50-80% (59), 60-65% (60)) triethyl methane-tricarboxylate (tricarbethoxymethane) [Beil. II-S10, II<sub>1</sub>-(320), II<sub>2</sub>-(680)], m.p.  $29^{\circ}$ , h.p.  $253^{\circ}$ ; note that this same prod. is also obtained (yields: 88-93% (61), 90% (62), 80% (63)) from  $\bar{C}$  with diethyl malonate (I:3581) in abs. alc. with Mg + trace  $CCl_4$ . —  $\bar{C}$  with the Na enolate of ethyl isobutyrate (I:3095) gives (75% yield (64)) diethyl dimethylmalonate (Beil. II-648, II<sub>1</sub>-(276), II<sub>2</sub>-(572)], b.p.  $195-196^{\circ}$  at 760 mm. — The reactn. of  $\bar{C}$  with ethyl sodioacetoacetate cannot be discussed here.]

[ $\bar{C}$  with excess RMgX compounds presumably gives first the corresp. esters which by further normal reactn. with more RMgX are converted to tertiary alcohols: e.g.,  $\bar{C}$  with EtMgBr (excess) yields (65) triethylcarbinol (I:6218); however, the intermediate ester can often readily be obtd.; e.g.,  $\bar{C}$  (1 mole) with *tert*-BuMgCl (1 mole) in dry ether gives (56% yield (66)) ethyl trimethylacetate (ethyl pivalate (I:3117), and other cases are recorded (66)); note, however, that with certain types of RMgX cpd. abnormal reactions can occur: e.g.,  $\bar{C}$  with benzyl MgCl yields not only the normal tribenzylcarbinol but also (67) ethyl *o*-toluate (I:3862). —  $\bar{C}$  also reacts with the  $=N-MgX$  grouping replacing  $-MgX$  by  $-COOEt$  (sometimes followed by rearrangement): e.g.,  $\bar{C}$  + 3,5-dimethylpyrrole-*N*-(magnesium bromide) gives (57-58% yield (68)) 5-carbethoxy-2,4-dimethylpyrrole.]

$\bar{C}$  also reacts readily with  $NH_3$ , with primary and secondary amines, with amino acids, etc., to replace one of the H's attached to N by the  $-COOEt$  group (see also below and under ⑥): e.g.,  $\bar{C}$  with excess conc. aq.  $NH_4OH$  immediately (if delayed, urea is formed) evaporated to dryness gives (3) ethyl carbamate (urethane) (Beil. III-22, III<sub>1</sub>-(9), III<sub>2</sub>-(19)], very eas. sol. aq., cryst. from abs. alc., dry ether,  $CHCl_3$ , or  $C_6H_6$ , m.p.  $48^{\circ}$ , b.p.  $184^{\circ}$ . — [ $\bar{C}$  (1 mole) in ether with 33% aq.  $MeNH_2$  soln. (1 mole) + aq. NaOH below  $5^{\circ}$  as directed (69) gives (88-90% yield (69)) (70) (71) ethyl *N*-methylcarbamate [Beil. IV-64, IV<sub>1</sub>-(330), IV<sub>2</sub>-(567)], oil, very sol. aq. (69 g. in 100 ml. aq. nt  $15.5^{\circ}$  (72)), b.p.  $170^{\circ}$ . — Countless other, analogous reactns. cannot be cited here.]

[ $\bar{C}$  with hydroxylamino hydrochloride + conc. aq.  $Na_2CO_3$  (73) or with dry  $K_2CO_3$  in ether (74) gives (89.6% yield (74)) *N*-hydroxyurethane (carbethoxyhydroxamic acid) (Beil. III-95, III<sub>2</sub>-(77)], oil, very sol. aq.]

$\bar{C}$  with hydrazine hydrate in alc. refluxed  $\frac{1}{2}$  hr. (75) (for starting with hydrazine sulfate see (76)) gives (yields: 100% (76), 90% (75)) diethyl *sym*-hydrazinedicarboxylate (*sym*-dicarbethoxyhydrazino) (Beil. III-98, III<sub>1</sub>-(46), III<sub>2</sub>-(79)], cryst. from hot aq., ndls. from  $CHCl_3$ , m.p.  $130^{\circ}$  (75),  $131^{\circ}$  (76) (note that the half reaction product, viz., ethyl hydrazinemonocarboxylate (*N*-aminourethane) (ethyl carbazinate), is also known (77) (78) but is an oil. —  $\bar{C}$  (1 mole) with urea (2.1 moles) refluxed for 2-3 hrs. gives (62-65% yield (79)) ethyl allophanate (*N*-carbethoxyurea) (Beil. III-69, III<sub>1</sub>-(31), III<sub>2</sub>-(56)], m.p.  $192^{\circ}$ .

$\bar{C}$  (1 mole) in ether with phenylhydrazine (2 moles) in ether (80) (81) (82) (76) or in aq. pyridine (83) gives (yields: 60-65% (80), 60% (76)) ethyl  $\omega$ -phenylcarbazinate ( $\beta$ -carb-

$\bar{C}$  has strong lachrymatory properties. — [For study of toxicity see (11).] —  $\bar{C}$  is comml. chemical in U.S.A.

[For prepn. of  $\bar{C}$  from carbonyl chloride (phosgene) (3:5000) with abs. EtOH (1:6130) (90% yield (12)) in pres. of dimethylaniline, quinoline, or antipyrine (13) or even  $\text{Ca}(\text{OH})_2$  (14) see indic. refs.; for formn. of  $\bar{C}$  from diethyl carbonate (1:3150) with  $\text{PCl}_5$  (15), from diethyl pyrocarbonate  $\text{O}(\text{COOEt})_2$  (16) with  $\text{SOCl}_2$  (17); from pentachloroethyl chloroformate [Beil. III-13, III-(6)] (18) or *bis*-(trichloromethyl) carboate (triphosgene) (3:1915) (19) or *bis*-(trichloromethyl) oxalate [Beil. III-17] (20) with EtOH, or from K xanthate, ethyl xanthate, or benzyl xanthate with  $\text{Cl}_2$  + aq. in cold (21) see indic. refs.]

Pyrolysis of  $\bar{C}$ .  $\bar{C}$  on htg at  $250^\circ$  decomposes yielding (4)  $\text{EtCl}$  (3:7015) +  $\text{CO}_2$  (for study of this reactn. see (22) (23)); in pres. of certain hydrocarbons or esters (24) or in pres. of dimethylaniline (25) temp. of this decomposition is lowered to  $150^\circ$ , in pres. of quinoline to  $59^\circ$  (26) (27), in pres. of  $\text{AlCl}_3$  to room temp. (28) (see also below under  $\bar{C}$  + pyridine or quinoline).

$\bar{C}$  in pres. of anhydrous  $\text{ZnCl}_2$  (29) (30) or even metallic Zn (31) decomposes at room temp. yielding (29) (30)  $\text{EtCl}$  (3:7015) + ethylene +  $\text{CO}_2$  +  $\text{HCl}$ .

Reactions of the  $-\text{COOC}_2\text{H}_5$  group of  $\bar{C}$ .  $\bar{C}$  on hydrolysis, e.g., by boilg. with aq. or dil. acid (32), yields  $\text{CO}_2$  +  $\text{HCl}$  + ethylene; on alkaline hydrolysis, however, no ethylene is formed (32); note that  $\bar{C}$  does not react with cold aq. very rapidly and may even be washed with it to remove alcohol.

[ $\bar{C}$  at its b.p. treated with  $\text{Cl}_2$  in sunlight undergoes further substitution by halogen yielding as final prod. (33) (31) pentachloroethyl chloroformate (ref. given above under prepn. of  $\bar{C}$ ).]

[ $\bar{C}$  with  $\text{EtHSO}_4$  at  $100^\circ$  under reflux for 6-8 hrs. gives (40% yield (48))  $\text{Et}_2\text{SO}_4$  +  $\text{EtCl}$  (3:7015).]

Reactions of the chlorine atom of  $\bar{C}$ . [ $\bar{C}$  on reduction with 3%  $\text{Na/Hg}$  + aq. gives (51% yield (35)) salt of formic acid (1:1005).]

[ $\bar{C}$  in  $\text{CHCl}_3$  with  $\text{Na}_2\text{O}_2$  does not react until 1-2 drops of aq. are added; vigorous actn. then ensues with formn. of the expected (but very explosive) dicarbethoxy peroxide ( $\text{EtOOC}-\text{O}-\text{O}-\text{COOEt}$ ) (36).]

[ $\bar{C}$  with  $\text{NaSH}$  (37) or with  $\text{C}_2\text{H}_5-\text{S}-\text{MgBr}$  (38 in ether gives (68% yield (38)) *O,S*-diethyl thiocarbonate [Beil. III-133, III-(62), III-(103)], b.p.  $158-159^\circ$  cor.;  $\bar{C}$  (2 moles) + aq. (39) or alc. (40)  $\text{Na}_2\text{S}$ ,  $\bar{C}$  with  $\text{BrMgSH}$  in ether (41), or  $\bar{C}$  with aq. potassium tri-thiocarbonate (39), gives diethyl thiodiformate (dicarbethoxy sulfide) [Beil. III-133, III-(103)], b.p.  $180^\circ$  dec.]

[ $\bar{C}$  with thallous fluoride 12 hrs. at room temp., then refluxed 2-3 hrs., gives (47% yield (42)) ethyl fluoroformate, lachrymatory oil, b.p.  $57^\circ$  (42).]

[For rate of reactn. of  $\bar{C}$  with  $\text{KI}$  in acetone at  $25^\circ$  see (43).]

[ $\bar{C}$  with aq. alc.  $\text{KCN}$  at  $-13^\circ$  (44) or with solid  $\text{NaCN}$  (contg. 0.2-7.0% moisture) at not above  $90^\circ$  (45) gives (yields: 90% (45), 46% (44)) ethyl cyanoformate [Beil. II-547, II-(238), II-(510)], b.p.  $115-116^\circ$  (46),  $D_4^{20} = 1.0034$  (47),  $n_D^{20} = 1.3821$  (47).]

$\bar{C}$  as carbethoxylating agent.  $\bar{C}$  is widely employed as a means of introducing the  $-\text{COOEt}$  group into other organic molecules by reactn. of the chlorine atom with the H of the alcoholic, phenolic, or enolic OH groups (or their metallic alcoholates, phenolates, enolates, etc.); under appropriate conditions  $\bar{C}$  is also employed to introduce the  $-\text{COOEt}$  group into an aromatic nucleus. Examples of these reactns. are cited below.

[ $\bar{C}$  with  $\text{NaOMe}$  yields (49) ethyl methyl carbonate [Beil. III-4, III-(4)], b.p.  $109^\circ$   $\bar{C}$  with  $\text{NaOEt}$  yields diethyl carbonate (1:3150); other alcohols behave similarly (50). —  $\bar{C}$  with K phenolate or  $\bar{C}$  with phenol in ether + dry  $\text{K}_2\text{CO}_3$  gives (71% yield (51)) ethyl phenyl carbonate [Beil. VI-157], b.p.  $229^\circ$ ; other mono-, di-, and polyhydric phenols behave

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ethoxy-phenylhydrazine) [Beil. XV-286, XV-(71)], cryst. from dil. alc. nr  $C_6H_6$ /lgr. as monohydrate, m.p.  $85^\circ$  (81) (82), anhydrous form, m.p.  $82-83^\circ$  (81),  $80-82^\circ$  (76). —  $\bar{C}$  with *p*-nitrophenylhydrazine in pyridine gives (84)  $\beta$ -carbethoxy-*p*-nitrophenylhydrazine, cryst. from alc., m.p.  $198-199^\circ$  (84). —  $\bar{C}$  with 2,4-dinitrophenylhydrazine in pyridine gives (84)  $\beta$ -carbethoxy-2,4-dinitrophenylhydrazine, cryst. from aq. alc., m.p.  $168-169^\circ$  (84).

$\bar{C}$  (1 mole) with pyridine (1 mole) in the cold gives first a colorless addn. prod. (85) which rapidly turns red (can be used as test for pyridine (85)) and on warming rapidly decomposes with evolution of  $CO_2$  +  $EtCl$  (3:7015);  $\bar{C}$  similarly treated with quinoline gives a yellow amorphous solid, considerably more stable than the above pyridine epd., but at  $100^\circ$  decomposing similarly but more slowly (85) in the same manner (see also above under pyrolysis).

① Ethyl *N*-phenylcarbamate (phenylurethane): ndls. from hot aq., tbls. from 90% alc., m.p.  $51.5-52^\circ$  (86),  $51-52^\circ$  (21) [From  $\bar{C}$  (1 mole) with aniline (2 moles) (86) (21) or from  $\bar{C}$  with aniline + cold aq.  $Na_2CO_3$  (87).] [For study of rate of this reactn. see (91).]

② Ethyl *N*-(*p*-tolyl)carbamate (*p*-tolylurethane): pr. from alc., m.p.  $52-53^\circ$  (21),  $52^\circ$  (88). [From  $\bar{C}$  (1 mole) with *p*-toluidine (2 moles) in ether (21) (88).]

③ *N,N'*-bis-(Benzyl)urea: ndls. from alc., m.p.  $167.5-169^\circ$  cor. (89). [From  $\bar{C}$  (1 ml.) with benzylamine (3 ml.) + trace  $NH_4Cl$  refluxed 1 hr. (89); note that in this reactn. (unlike the two preceding cases) the reagent amino not only reacts with the chlorine atom of  $\bar{C}$  but also ammonolyzes the carbethoxy group; the prod. is therefore a disubstituted urea rather than the ethyl *N*-benzylcarbamate [Beil. XII-1049], lfts. from lgr., m.p.  $48-49^\circ$  (90), which is formed from  $\bar{C}$  + benzylamine + cold aq.  $NaOH$  (90).]

— *N*-(Carbethoxy)phthalimide: unreported.

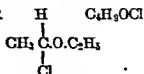
— *N*-(Carbethoxy)-3-nitrophthalimide: unreported.

— *N*-(Carbethoxy)-tetrachlorophthalimide: unreported. [Note that  $\bar{C}$  with  $K$  tetrachlorophthalimide fails to react under reflux and explodes on htg. in a.t. (92).]

— *S*-(Carbethoxy)isothioureia picrate: m.p.  $150-151^\circ$  (93). [Note that  $\bar{C}$  (1 mole) with thiourea (1 mole) in conc. aq. soln. on treatment with  $NaHCO_3$  in slight excess evolves  $CO_2$  and ppts. *S*-(carbethoxy)isothioureia bicarbonate, bulky white ppt., insol. aq., m.p.  $59-60^\circ$  dec.; this ppt. on immediate treatment with dil.  $HCl$  dissolves and from the solution  $PkOH$  gives *S*-(carbethoxy)isothioureia picrate; the same prod. may also be obt'd. from the original aq. soln. of  $\bar{C}$  + thiourea by direct addn. of  $PkOH$  (93). — Note, however, that the above bicarbonate on stdg. with aq. changes spontaneously to *N,N*-dicarbethoxythioureia, m.p.  $97^\circ$  dec., + thiourea. — Note, however, that  $\bar{C}$  (1 g.) with thiourea (1 g.) in  $EtOH$  (10 ml.) refluxed 30 min., then treated with  $PkOH$  (1 g.) does not yield the above prods. but instead (94) *S*-ethyl-isothioureia picrate, m.p.  $187^\circ$  (94).]

3:7295 (1) Timmermans, *Bull. soc. chim. Belg.* **31**, 392 (1922). (2) Perkin, *J. Chem. Soc.* **65**, 420 (1894). (3) Dumas, *Ann. chim.* (2) **54**, 225-237 (1833); *Ann.* **19**, 277-288 (1834). (4) Pavlevski, *Ber.* **25**, 1419-1451 (1892). (5) Forster, Newman, *J. Chem. Soc.* **97**, 2573 (1910). (6) Karvonen, *Ann. Acad. Sci. Fennicae A-10*, No. 4, 19; *Cent.* **1919**, III 808. (7) Mizushima, Kudo, *Bull. Chem. Soc. Japan* **13**, 178 (1938). (8) Guye, Mallet, *Arch. sci. phys. Nat. Genève* (4) **13**, 274-290; *Cent.* **1902**, I 1315. (9) von Auwers, *Ber.* **60**, 2140 (1927). (10) Jaeger, *Z. anorg. allgem. Chem.* **101**, 67 (1917).

**3:7305  $\alpha$ -CHLOROETHYL ETHYL ETHER**  
( $\alpha$ -Chlorodiethyl ether;  
 $\alpha$ -ethoxyethyl chloride)

 $\text{C}_4\text{H}_9\text{OCl}$ 

Beil. I - 606  
I<sub>1</sub>-(327)  
I<sub>2</sub>-

B.P. 97.5° cor. at 750 mm. (1)

 $D_4^{20} = 0.9537$  (1) $n_D^{20} = 1.3950$  (1)

93-94° at 735 mm. (2)

0.9655 (3)

1.4052 (3)

Colorless liq. which fumes in moist air.

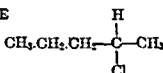
[For prepn. (94% yield (1); 69% yield (6)) from paraldehyde (1:0170) + ethyl alc. (1:6130) + dry HCl see (1) (4); for prepn. (78% yield (5)) from acetaldehyde (1:0100) + ethyl alc. (1:6130) + dry HCl see (2) (5).]

 $\bar{C}$  on stdg. polymerizes to dark tarry residue (1). $\bar{C}$  on bromination yields  $\alpha,\beta$ -dibromoethyl ethyl ether (6) (7)(5).

$\bar{C}$  on shaking with aq. yields acetaldehyde (1:0100), ethyl alc. (1:6130), + HCl; for study of rate of hydrolysis see (8).

**3:7305** (1) Henze, Murchison, *J. Am. Chem. Soc.* **53**, 4077-4079 (1931). (2) Mohler, Sorge, *Hds. Chim. Acta* **23**, 1209 (1940). (3) Waterman, de Kok, Leendertse, Schoenmaker, *Rec. trav. chim.* **56**, 437-441 (1937). (4) de Kok, Leendertse, Waterman, *Chem. Weekblad*, **37**, 579-583 (1940); *C.A.* **36**, 4800 (1942). (5) Sherrill, Walter, *J. Am. Chem. Soc.* **58**, 743 (1936). (6) Swallen, Boord, *J. Am. Chem. Soc.* **52**, 654 (1930). (7) Dykstra, Lewis, Boord, *J. Am. Chem. Soc.* **52**, 3400 (1930). (8) Mohler, Hartnagel, *Hds. Chim. Acta* **25**, 859-863 (1942); *C.A.* **37**, 1799 (1943).

**3:7325 *d,l*-2-CHLOROPENTANE**  
(*sec*-(2)Amyl chloride;  
methyl-*n*-propylcarbonyl  
chloride)

 $\text{C}_5\text{H}_{11}\text{Cl}$ 

Beil. I - 131  
I<sub>2</sub>-( 43)  
I<sub>2</sub>-( 95)

B.P.

F.P.

97° at 770 mm. (16)

-139 to -137° (1)

 $D_4^{20} = 0.8732$  (16)

96.84-96.88° at 760 mm. (1)

0.8695 (1)

96.6-96.8° at 760 mm. (2)

96.87-96.96° at 759 mm. (5)

 $n_D^{20} = 1.40791$  (16)

96.7° at 760 mm. (14)

1.4009 (1)

95.9-96.6° (3)

1.4068 (4)

95.5-96.0° at 755 mm. (4)

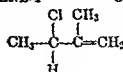
95° at 729 mm. (1)

Note that all samples of  $\bar{C}$  reported prior to 1935 were undoubtedly mixts. of 2-chloropentane ( $\bar{C}$ ) with 3-chloropentane (3:7330). Each of these cpds. is with great ease partially converted to the other (see text), and their mixt. cannot be separated by fractional distillation (1).

[For prepn. of  $\bar{C}$  (or its mixt. with 3-chloropentane (3:7330)) from pentanol-2 (1:6185) with conc. HCl on long stdg. at room temp. (78% yield (1)) or in s.t. at 110° (3) see (1) (2) (3); with conc. HCl +  $\text{ZnCl}_2$  (yield: 70% (6), 49% (16)) see indic. refs.; with  $\text{PCl}_3$  +  $\text{ZnCl}_2$  (64% yield (6)) or  $\text{PCl}_5$  +  $\text{ZnCl}_2$  (56% yield (6)) see (6); with  $\text{SOCl}_2$  + pyridine (gives least rearr. (1)) (yield: 28% (1), 67% (6)) see (1) (6); from pentene-2 on shaking 10 hrs. at room temp. with conc. HCl see (5) (4).] [Note that both pentanol-2 (1:6185) and pentanol-3 (1:6175) with HCl even at room temp. give mixts. of 2-chloropentane ( $\bar{C}$ ) and 3-chloropentane (3:7330) (11).] [For formn. of  $\bar{C}$  in small amt. during reactn. of pentanol-1 (1:6205) with HCl +  $\text{ZnCl}_2$  see (15).]

**3: 7300 d,l-3-CHLORO-2-METHYLBUTENE-1**  
 ( $\alpha,\beta$ -Dimethylallyl chloride)
 $C_5H_9Cl$ 

Beil. I - 211

I<sub>1</sub> - ( 87)I<sub>2</sub> -
 B.P. 93.8° at 760 mm. {1}  
 18.0-18.1° at 30 mm. {1}
 $D_4^{20} = 0.9088$  {1} $n_D^{20} = 1.4304$  {1}

Note:  $\bar{C}$  by virtue of facile allylic transposition is in equilibrium with its synionic isomer, 1-chloro-2-methylbutene-2 (3:7485); reactns. of  $\bar{C}$  may therefore yield also derivatives related to its isomer.

[For prepn. of  $\bar{C}$  (or its mixt. with 1-chloro-2-methylbutene-2) by actn. of  $Cl_2$  as specified {1} on "tertiary amylene" (a mixt. consisting mainly of 2-methylbutene-2 (1:8220) with some 2-methylbutene-1 (1:8210)) see {1}. — The relative amt. of  $\bar{C}$  and its isomer is not constant but usually is about 60% of  $\bar{C}$  with 40% of 1-chloro-2-methylbutene-2, the ratio, however, being independent of the proportion of the two olefins in the starting material.]

[For formn. of  $\bar{C}$  from 2-methylbutene-2 (1:8220) with  $Cl_2$  see {2}; from 2-methylbutene-1 (1:8210) see {3}; from 2,3-dichloro-2-methylbutane (3:7975) + alc. KOH {3} or by thermal dehydrohalogenation at 420-450° {4} see indic. refs.]

$\bar{C}$  on hydrolysis gives not only the corresponding alc. but also that corresponding to the isomeric 1-chloro-2-methylbutene-2 (3:7485) together with a little isopropyl methyl ketone. For details see the isomer (3:7485).

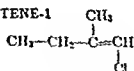
$\bar{C}$  with HCl yields {2} 2,3-dichloro-2-methylbutane (3:7975) + 1,3-dichloro-2-methylbutane (3:9228).

$\bar{C}$  adds  $Br_2$  giving {3} 1,2-dibromo-3-chloro-2-methylbutane, m.p. 197-198° {3}.

**3: 7300** {1} Burgin, Engs. Groll, Hearne, *Ind Eng Chem* **31**, 1416-1417 (1939). {2} Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **6**, 1116-1132 (1936), *Cent.* 1937, I 572; *C.A.* **31**, 1003 (1937). {3} Gutner, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **8**, 1062-1067 (1938), *Cent.* 1939, II 4221; *C.A.* **33**, 3755 (1939). {4} Due, Nuessig (to Standard Oil Development Co.) U.S. 2,332,778, Oct. 26, 1943, *C.A.* **39**, 1750 (1944).

**3: 7303 1-CHLORO-2-METHYLBUTENE-1**
 $C_5H_9Cl$ 

Beil. I —

I<sub>1</sub> —I<sub>2</sub> - (187)

B.P. 96-97° {1}

 $D_4^{20} = 0.9170$  {1}

Oil with agreeable odor. — Insol. aq., sol. ether.

[For prepn. of  $\bar{C}$  from 1-chloro-2-methylbutanol-2 (3:8175) by loss of  $H_2O$  on distn. with anhyd. oxalic acid (1:6535) (11% yield {1}) together with other prods.), or on treatment with  $PCl_5$  {2} or  $Ac_2O$  + trace conc.  $H_2SO_4$  {2} see indic. refs.; for formn. of  $\bar{C}$  from 2-methylbutanedial-1,2 with  $PCl_5$  {2} or from 1,2-epoxy-2-methylbutane ( $\alpha$ -ethyl- $\alpha$ -methylene oxide) with  $PCl_5$  (1 mole) in cold {1} {2} or with  $SOCl_2$  {2} see indic. refs.]

[ $\bar{C}$  with  $PCl_5$  adds  $Cl_2$  yielding {2} a cpd.  $C_5H_9Cl_3$ , b.p. 180-184°.]

$\bar{C}$  adds  $Br_2$  readily {2}.

[For behavior of  $\bar{C}$  with NaI in acetone see {1}.]

**3: 7303** {1} Chalmers, *Trans Roy Soc. Can.* (3) **22**, III 75-78 (1925); *Cent.* 1929, I 631-632; *C.A.* **23**, 2694 (1929). {2} Feyer, Chalmers, *Trans Roy Soc. Can.* (3) **20**, III 334-339 (1926); *Cent.* 1927, II 1411, *C.A.* **21**, 2663 (1927).



$\bar{C}$  is stable (no change in  $n_D^{20}$ ) on htg. in s.t. at 100° for 48 hrs. (1). — However,  $\bar{C}$  on shaking at 26-28° for 24 hrs. with HCl + ZnCl<sub>2</sub> gives a mixt. consisting of 20%  $\bar{C}$  + 80% 2-chloropentane (1).

[For study of rate of hydrolysis by water at 80° and 180° and rate of cleavage of HCl at 180° see (12).]

Ⓔ Diethylacetanilide:  $\bar{C}$  with Mg in dry ether yields R.Mg.Cl which, upon reactn. with phenyl isocyanate and subsequent hydrolysis, yields (1) (3) (4) (5) diethylacetanilide, m.p. 127.5° (8), 126.8° (9), 126-127° (5), 125-128° (1), 123-124° cor. (10), 122° (3), 121° (11). [For m.p./compn. data and diagrams for mixts. of diethylacetanilide (from  $\bar{C}$ ) with methyl-*n*-propylacetanilide (from 2-chloropentane) see (4) (3) (11)] [For crystallographic study of these two anilides see (13).]

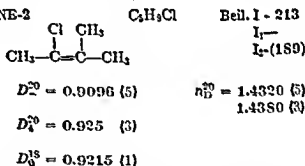
Ⓕ Diethylacet-*p*-toluidide: m.p. 107.5-108.5° u.c. (5), 116.2° (9).

Ⓖ Diethylacet- $\alpha$ -naphthalide: m.p. 117-118° u.c. (5).

3:7330 (1) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2536-2538 (1938). (2) Hass, *J. Chem. Education* 13, 493 (1936). (3) Hass, Weber, *Ind. Eng. Chem., Anal. Ed.* 7, 231-233 (1935). (4) Kharasch, Walling, Mayo, *J. Am. Chem. Soc.* 61, 1559-1564 (1939). (5) Underwood, Gale, *J. Am. Chem. Soc.* 56, 2117-2120 (1934). (6) Koelsch, McElvain, *J. Am. Chem. Soc.* 52, 1161-1169 (1930). (7) Clark, Streight, *Trans. Roy. Soc. Can.* (3) 23, 111 77-89 (1929). (8) Tiffeneau, *Compt. rend.* 204, 592 (1937). (9) Hommelen, *Bull. soc. chim. Belg.* 42, 249 (1933). (10) Schwartz, Johnson, *J. Am. Chem. Soc.* 53, 1065 (1931).

(11) Lauer, Stodola, *J. Am. Chem. Soc.* 56, 1218 (1934). (12) Ayres, *Ind. Eng. Chem.* 21, 899-904 (1929). (13) Whitmore, Karnatz, Popkin, *J. Am. Chem. Soc.* 60, 2541 (1938). (14) Vogel, *J. Chem. Soc.* 1943, 638, 640.

3:7335 3-CHLORO-2-METHYLBUTENE-2  
(Trimethylvinyl chloride)



[For prepn. of  $\bar{C}$  from isopropyl methyl ketone (1:5410) with PCl<sub>5</sub> see (3) (4); from 3-chloro-2-methylbutanol-2 (3:8030) by dehydration with P<sub>2</sub>O<sub>5</sub> (50% yield (1)), anhyd. oxalic acid (6) at 130°, or strong oxygenated mineral acids such as H<sub>2</sub>SO<sub>4</sub> (92% yield (7)) see indic. refs.]

[For formn. of  $\bar{C}$  (together with other prods.) from 2,3,3-trichloro-2-methylbutane (3:4755) (8) or from 2,3-dichloro-2-methylbutane (3:7975) with alc. KOH (2), from 2-methylbutene-2 (1:8210) with Cl<sub>2</sub> + NaHCO<sub>3</sub> at 0° (70-80% yield (9)) or with *tert*-butyl hypochlorite (3:7165) (47.5% yield (5)), or from 2-methylbutanol-2 (1:6160) with Cl<sub>2</sub> (10) see indic. refs.]

$\bar{C}$  with Cl<sub>2</sub> + NaHCO<sub>3</sub> at 0° gives (9) 80% 3,3-dichloro-2-methylbutene-1 (3:7690) + 10% addn. prod. 2,3,3-trichloro-2-methylbutane (3:4755).

$\bar{C}$  in cold ether adds Br<sub>2</sub> giving (1) (2) 2,3-dibromo-3-chloro-2-methylbutane, cryst. m.p. 197° (1), 197-198° (2).

3:7335 (1) Krassuski, *J. Russ. Phys.-Chem. Soc.* 33, 15-17 (1901); *Cent.* 1901, I 935. (2) Gutner, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1062-1067 (1938); *Cent.* 1939, II 4221; *C.A.* 33, 3755 (1939). (3) Gredy, *Bull. soc. chim.* (5) 2, 1951 (1935). (4) Béhal, *Ann. chim.* (6) 15, 284-285

$\bar{C}$  is stable (no change in  $n_D^{20}$ ) on htg. in a.t. at 100° for 48° (1). — However,  $\bar{C}$  on shaking at 26–28° for 24 hrs. with HCl + ZnCl<sub>2</sub> gives a mixt. consisting of 80%  $\bar{C}$  + 20% 3-chloropentane (3:7330) (1).

[For study of rate of hydrolysis by water at 80° and 180° see (7); for rate of reactn. with KI in acetone at 60° see (8); for reactn. with Na see (9).]

⑩ Methyl-*n*-propyl-acetanilide:  $\bar{C}$  with Mg in dry ether yields RMgCl which upon reactn. with phenyl isocyanate and subsequent hydrolysis yields (1) (2) (4) (10) methyl-*n*-propyl-acetanilide, m p. 94-96° (1), 95.2° (11), 92.6° (12), 92.5° (2), 88° cor. (13). [For m.p./compn. data and diagrams for mixts. of methyl-*n*-propyl-acetanilide (from  $\bar{C}$ ) with diethylacetanilide (from 3-chloropentane) see (4) (2) (12).] [For crystallographic study of these two anilides see (15).]

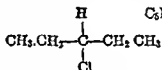
① Methyl-*n*-propyl-acet-*p*-toluidide: m.p. 90-92° u c. (10); 80.5° (11).

⑪ Methyl-*n*-propyl-acet- $\alpha$ -naphthalide: m.p. 102.5–103.5° (10).

3:7325 (1) Whitmore, Karnatz, *J. Am. Chem. Soc.* **60**, 2536-2538 (1938). (2) Hass, Weber, *Ind. Eng. Chem., Anal. Ed.* **7**, 231-233 (1935). (3) Kohlrausch, Köppl, *Monatsh.* **65**, 195 (1935). (4) Kharasch, Walling, Mayo, *J. Am. Chem. Soc.* **61**, 1559-1564 (1939). (5) Norris, Reuter, *J. Am. Chem. Soc.* **49**, 2630-2631 (1927). (6) Clark, Streight, *Trans. Roy. Soc. Can.* (3) **23**, 111 77-89 (1929). (7) Ayres, *Ind. Eng. Chem.* **21**, 899-904 (1929). (8) Conant, Hussey, *J. Am. Chem. Soc.* **47**, 485 (1925). (9) Morton, LeFevre, Hechenbleikner, *J. Am. Chem. Soc.* **58**, 757 (1936). (10) Underwood, Gale, *J. Am. Chem. Soc.* **56**, 2117-2120 (1934). (11) Hommelen, *Bull. soc. chim. Belg.* **42**, 249 (1933). (12) Lauer, Stodola, *J. Am. Chem. Soc.* **56**, 1218 (1934). (13) Schwartz, Johnson, *J. Am. Chem. Soc.* **53**, 1965 (1931). (14) Hass, *J. Chem. Education* **13**, 492-493 (1936). (15) Whitmore, Karnatz, Popkin, *J. Am. Chem. Soc.* **60**, 2541 (1938). (16) Vogel, *J. Chem. Soc.* **1943**, 638, 649.

## 3:7330 3-CHLOROPENTANE

(sec.-(3) Amyl chloride;  
diethylcarbinyl chloride)



Beil. I - 131

$I_2 = (95)$

B.P.

97.76–97.82° at 760 mm. (1)

97.3° at 760 mm. (2)

F.P.

-105 to -106° (1)

0.8723 (14)

0.8795 (1)  
0.8723 (14)

97.1-97.4<sup>a</sup> at 760 mm. (3)

96.8-97.2° at 755 mm. (4)

96.7-97.1° at 758 mm. (5)

96° at 753 mm. (14)

96-97° at 729 mm. (6)

$$n_D^{20} = 1.4104 \quad (1)$$

1.4103 (4)

1.40820 (14)

Note that all samples of  $\tilde{C}$  reported prior to 1935 were undoubtedly mixts. of 3-chloropentane ( $\tilde{C}$ ) with 2-chloropentane (3:7325). Each of these cpds. is with great ease partially converted to the other (see text), and the mixture cannot be separated by fractional distillation (1).

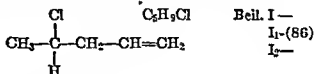
[For prepn. of **6** (or its mixture with 2-chloropentane (3:7325)) from pentanol-3 (1:6175) with conc. HCl on long stdg. at room temp. (yield: 84% (1); 69% (3)) see (1) (3); with dil. HCl see (5); with conc. HCl +  $\pi$ -C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> (9:10) or  $\pi$ -C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> (9:10) see (1) (3); with PCl<sub>3</sub> + ZnCl<sub>2</sub> (60% yield) with pyridine gives least rearr. (1)]

(1:8215) + HCl in presence of  $\text{FeCl}_3$  or  $\text{AcOH}$  see (4).] [Note that both pentanol-2 (1:6185) and pentanol-3 (1:6175) with HCl even at room temp. give mixts. of 2-chloropentane (3:7325) and 3-chloropentane ( $\bar{\text{C}}$ ) (1).] [For formn. of  $\bar{\text{C}}$  in small amt. during reactn. of pentanol-1 (1:6205) with HCl +  $\text{ZnCl}_2$  see (12).]

For anal. of mixts. of  $\bar{C}$  with 1-chloro-3-methylbutane (3:7365) via rate of reactn. with KI in acetone see (2).

$\bar{C}$  with Mg in dry ether does not react (8). [However, from corresp. *d,l*-sec.-butyl-carbinyl bromide the R.Mg.Br epd. was obtd. (9) in 66% yield and with phenyl isocyanate yielded *N*-(sec.-butylacet)anilide, m.p. 88° cor. (9), 87° (10).]

3:7345 (1) Hass, McBee, Weber, *Ind. Eng. Chem.* 27, 1192-1195 (1935). (2) Hass, Weber, *Ind. Eng. Chem., Anal. Ed.* 7, 231-233 (1935). (3) Kohlrausch, Köppl, *Monatsh.* 65, 195 (1935). (4) Ayres, *Ind. Eng. Chem.* 21, 900 (1929). (5) Brauns, *J. Research Natl. Bur. Standards* 18, 323-324, 327-328 (1937). (6) Whitmore, Olewine, *J. Am. Chem. Soc.* 60, 2570-2571 (1938). (7) Brown, Kharasch, Chao, *J. Am. Chem. Soc.* 62, 3439 (1940). (8) Underwood, Gale, *J. Am. Chem. Soc.* 56, 2117 (1934). (9) Schwartz, Johnson, *J. Am. Chem. Soc.* 53, 1063-1068 (1931). (10) Hommelen, *Bull. soc. chim. Belg.* 42, 249 (1933).  
(11) Brown, Groot, *J. Am. Chem. Soc.* 64, 2566 (1942).

3:7350 *d,l*-4-CHLOROPENTENE-1

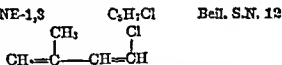
B.P. 97-100° (1)

 $D_4^{15} = 0.934$  (1) $n_D^{15} = 1.417$  (1)

The levorotatory form of  $\bar{C}$  has  $D_4^{25} = 0.5794$  (2),  $n_D^{25} = 1.4218$  (2), but no b.p. or method of prepn. is recorded.

[For prepn. of  $\bar{C}$  from penten-1-ol-4 (allyl-methyl-carbinol) (Beil. I-443) with  $\text{PCl}_5$  at 0° see (1).]

3:7350 (1) Pariselle, *Compt. rend.* 154, 712 (1912). (2) Levene, Rothen, *J. Chem. Phys.* 5, 982 (1937).

3:7355 1-CHLORO-3-METHYLBUTADIENE-1,3  
(4-Chloro-2-methylbutadiene-1,3)

B.P. 99-100° (1)

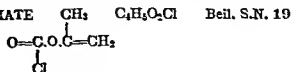
 $D_4^{20} = 0.9543$  (1) (2) $n_D^{20} = 1.47189$  (1)

97.5-98° (2)

[For prepn. of  $\bar{C}$  from 1-chloro-3-methylbutadiene-1,2 (3:7390) by stdg. several days with  $\text{HCl} + \text{Cu}_2\text{Cl}_2 + \text{NH}_4\text{Cl}$  see (2).]

$\bar{C}$  without solvent on htg. with maleic anhydride (1:0625) evolves  $\text{HCl}$  and gives (1) a mixt. of 4 acids; 2 dicarboxylic acids, m.p. 210-211° (1) (2) and m.p. 239-241° (1), and 2 tetracarboxylic acids, m.p. 298-299° (1) and m.p. 352-353° (1) (2); with solvent only the acids of m.p. 210-211° and 352-353° are formed (2):

3:7355 (1) Favorskii, Favorskaya, *Compt. rend.* 200, 839-840 (1935); *Cent.* 1935, II 1340; *C.A.* 29, 3651 (1935). (2) Favorskii, Favorskaya, *J. Gen. Chem. (U.S.S.R.)* 9, 386-395 (1939); *C.A.* 33, 9251 (1939).

3:7358 ISOPROPENYL CHLOROFORMATE  
(Isopropenyl chlorocarbonate)

B.P.

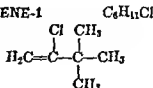
at 760 mm. (estimated) (1)

 $D_{20}^{20} = 1.103$  (1)

at 746 mm. (1)

10, 381 (1897)

3:7340 2-CHLORO-3,3-DIMETHYLBUTENE-1  
(3-Chloro-2,2-dimethylbutene-3)



Beil. I - 218  
I<sub>1</sub>—  
I<sub>2</sub>-(195)

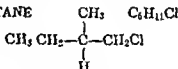
B.P. 98° (1)  
97-99° (2)

[For prepn. of  $\bar{C}$  from *ter*-butyl methyl ketone (pinacolone) (1 5425) with  $\text{PCl}_5$  on htg. (1) (50% yield (3)) or from 3,3-dichloro-2,2-dimethylbutane (3 4325) on htg. with alc. KOH at 150° (1) (3) or with KOAc + phenol (4) see indic. refs.]

$\bar{C}$  with alc. KOH (3) or htd. at 160-200° for 5 hrs. with powdered KOH (or NaOH (5)) moistened with alc. (2) gives (80.5% yield (2)) *ter*-butylacetylene [Beil. I-256], b.p. 36.4-37.8° at 768.3 mm. (2).

3:7340 (1) Delacro, *Bull. acad. roy. Belg* 1906, 7-41; *Cent* 1906, I 1233. (2) Bartlett, Rosen, *J. Am. Chem. Soc.* 64, 544 (1942). (3) Delacro, *Bull. soc. chim.* (3) 35, 313-344 (1906). (4) Meerwein, Wortmann, *Ann.* 435, 194, Note 1 (1924). (5) de Græf, *Bull. soc. chim. Belg.* 34, 429 (1925).

3:7345 *d,l*-1-CHLORO-2-METHYLBUTANE  
(*d,l*-*sec.*-Butylcarbinyl chloride)



Beil. I - 134  
I<sub>1</sub>-(46)  
I<sub>2</sub>-(100)

B.P.

99.9° at 760 mm. (1) (2)

99.8-100° at 760 mm. (2)

99.5-100.5° (3)

99° (4)

52.5° at 150 mm. (1)

$D_4^{20}$  unrecorded  
(See note below.)

$n_D^{20}$  unrecorded  
(See note below.)

[Note: for active *d* stereoisomer: b.p. 100.45° at 760 mm (5), 99.5° at 750 mm. (11), 86.8° at 500 mm (5), 80.0° at 400 mm. (5), 71.5° at 300 mm. (5), 60.4° at 200 mm. (5), 43.0° at 100 mm. (5), 27.7° at 50 mm. (5);  $D_4^{20}$  9.8857 (5), 0.8852 (6),  $n_D^{20} = 1.4124$  (5), 1.4125 (6), 1.4126 (11)]

The sepn. of  $\bar{C}$  from 4-chloro-2-methylbutane (isoamyl chloride) (3:7365) by fractional distillation cannot be effected (1) (2).

[For prepn. of  $\bar{C}$  from the corresponding alc., *d,l*-*sec.*-butylcarbinol (cf. 1:6195) with HCl gas at 90° for 6 hrs. (49% yield) see (2); with  $\text{SOCl}_2$  see (3); for prepn. of *d*-form from corresp. alc. (1:6195) by satn. at 0° with HCl gas and htg. in s.t. 5 hrs. at 100° (20% yield) see (5), by use of  $\text{SOCl}_2$  + pyridine (yield: 87% (11), 82% (7), 77% (6)) see (6) (7).]—  
[For formn. by chlorination of crude pentane see (4).]

$\bar{C}$  is not hydrolyzed by aq. either at 80° or at 180° (4). — For rate of loss of HCl at 180° to yield 2-methylbutene-1, b.p. 31° (1:8210), see (4).

3:0560 (1) Holleman, *Rec. trav. chim.* 37, 96-107 (1918). (2) van de Lande, *Rec. trav. chim.* 51, 103, 110 (1932). (3) Kohlrausch, Stockmair, Ypsilanti, *Monatsh.* 67, 89 (1936). (4) Fischer, *Ann. Suppl.* 7, 180-190 (1870). (5) Lock, *Monatsh.* 55, 311-312 (1930). (6) Groves, Turner, *Chem. J. Chem. Soc.* 1930, 516-518, 521-522, 523-524 (1930).

(11) Chandelon, *Ber.* 16, 1751-1752 (1883). (12) Chulkov, Parini, Staroselets, *Org. Chem. Ind. (U.S.S.R.)* 3, 97-101 (1937); *Cent.* 1933, I 1419; *C.A.* 31, 4967 (1937). (13) Likhoherstov, *J. Russ. Phys.-Chem. Soc.* 61, 1019-1023, 1025-1028 (1929); *Cent.* 1930, I 1294; *C.A.* 24, 836 (1930). (14) Steinkopf, Mieg, Herold, *Ber.* 53, 1145 (1920). (15) Tarugi, *Gazz. chim. ital.* 30, II 489, 491 (1900). (16) Hecht, *Am. Chem. J.* 12, 505 (1890). (17) Zinke, *Ann.* 261, 253-254 (1891). (18) Garzino, *Gazz. chim. ital.* 17, 495-503 (1887). (19) Rox, Turner, *J. Chem. Soc.* 1930, 1861-1863. (20) Kohn, Dömötör, *Monatsh.* 47, 215-216 (1926).

(21) Armstrong, *J. Chem. Soc.* 25, 96 (1872). (22) Kohn, Kramer, *Monatsh.* 49, 156 (1928). (23) Buehler, Brown, Holbert, Fulmer, Parker, *J. Org. Chem.* 6, 905-906 (1941). (24) Ziegler, Simmler, *Ber.* 74, 1871-1879 (1941). (25) Weiler, Wenk, Stötter, *Ger.* 540,208, Dec. 12, 1931; *Brit.* 337,832, Dec. 4, 1930; *French* 39,334, Oct. 12, 1931; *Cent.* 1932, I 3013. (26) Weiler, Wenk, Stötter, *U.S.* 1,707,181, March 26, 1929; *French* 651,646, Feb. 21, 1929; *Cent.* 1929, II 499. (27) I.G., Austrian 118,640, July 25, 1930; *Cent.* 1930, II 2978. (28) I.G., Swiss 134,012, Sept. 2, 1929; *Cent.* 1930, I 1876. (29) I.G., *Brit.* 334,847, Oct. 9, 1930; *Cent.* 1931, II 618. (30) I.G., *Brit.* 337,473, Nov. 27, 1930; *Cent.* 1931, I 2233.

(31) Muth (to I.G.), *Ger.* 583,055, Aug. 28, 1933; *Cent.* 1933, II 3883. (32) I.G., Swiss 137,923-137,929; 138,180-138,183, April 16, 1930; *Cent.* 1930, II 1453. (33) I.G., Swiss 143,330, Oct. 1, 1931; *Cent.* 1932, I 1845. (34) Weiler (to I.G.), *Ger.* 548,822, April 20, 1932; *Cent.* 1932, II 799. (35) Weiler, Retter (to I.G.), *Ger.* 604,950, Nov. 3, 1934; *Cent.* 1935, I 1150. (36) Ullmann, Conzetti, *Ber.* 53, 827, 831-832 (1920). (37) Scottish Dyes, Ltd. + Thomas + Hooley, *Brit.* 234,533, June 25, 1925; *Cent.* 1926, I 245. (38) Ullmann, *Ger.* 282,493, March 6, 1915; *Cent.* 1915, I 643. (39) Zahn, *Ber.* 67, 2078 (1934). (40) Scottish Dyes, Ltd. + Bangham, Hooley, Thomas, *Brit.* 339,559, Jan. 8, 1931; *Cent.* 1932, I 2035.

(41) Hantzsch, *Ber.* 32, 3070 (1899). (42) Murray, Gordon, *J. Am. Chem. Soc.* 57, 110-111 (1935). (43) Ordal, *Proc. Soc. Exptl. Biol. Med.* 47, 387-389 (1941); *C.A.* 35, 6061 (1941). (44) Ellis (to Insulite Co.), *U.S.* 2,161,654, June 6, 1939; *Cent.* 1939, II 4620. (45) I.G., *Brit.* 356,192, Oct. 1, 1931; *Cent.* 1931, II 3360. (46) Simonis, Schuhmann, *Ber.* 50, 1148 (1917). (47) Lock, *Monatsh.* 62, 184-185 (1933). (48) Birosel, *J. Am. Chem. Soc.* 53, 1408-1412 (1931). (49) Goldsworthy, *J. Chem. Soc.* 1926, 1254-1256. (50) Raiford, Howland, *J. Am. Chem. Soc.* 53, 1055 (1931).

(51) Chien, Yin, *J. Chinese Chem. Soc.* 7, 40-45 (1939); *C.A.* 34, 1979 (1940). (52) Bradfield, Jones, *J. Chem. Soc.* 1931, 2906. (53) von Auwers, *Ann.* 357, 92-93 (1907). (54) Baw, *J. Indian Chem. Soc.* 3, 104 (1926). (55) Huston, Eldredge, *J. Am. Chem. Soc.* 53, 2263 (1931). (56) Bost, Nicholson, *J. Am. Chem. Soc.* 57, 2368-2369 (1935). (57) Raiford, Thiessen, Wernert, *J. Am. Chem. Soc.* 52, 1208 (1930). (58) Pokorny, *J. Am. Chem. Soc.* 63, 1768 (1941). (59) Zimmermann, *Ind. Eng. Chem.* 35, 597-599 (1943). (60) Zimmermann, Hitchcock, *Contrib.*

(62) Sah, Cheng,  
-599 (1939). (64)

Sah, *Rec. trav. chim.* 58, 587-589 (1939). (65) Sah, *Rec. trav. chim.* 58, 454-458 (1939).

Colorless lachrymatory liq. with sharp and unpleasant odor.

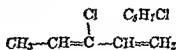
[For prepn. of  $\bar{C}$  from acetone (1:5400) with liq. phosgene (3:5000) for  $\frac{1}{2}$  hr. at room temp. see (1).]

3:7358 (1) Matuszak, *J. Am. Chem. Soc.* 56, 2007 (1934).

3:7360 3-CHLOROPENTADIENE-1,3

("Methylchloroprene";

pyrylene monohydrochloride)



Beil. S.N. 12

B.P.  
99.5-101.5° at 759 mm. (1) (2)  $D_4^{20} = 0.9576$  (1) (2)  $n_D^{25} = 1.4745$  (3)  
98.5-101° (3)  $n_D^{20} = 1.4785$  (1) (2)

Colorless liq. with characteristic odor; after addition of hydroquinone (as antioxidant) can be distilled (1). — [For polymerization of  $\bar{C}$  see (1) (2).]

[For prepn. of  $\bar{C}$  from penten-1-yne-3 ( $\alpha$ -methyl- $\beta$ -vinylacetylene = pyrylene (3)) by shaking with conc. HCl contg. CuCl + NH<sub>4</sub>Cl see (1) (2) (3).]

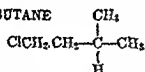
$\bar{C}$  on htg. with 1,4-naphthoquinone (1:9040) at 100° for 2 hrs. then treated with alc. NaOH, and aerated (to oxidize the intermediate addn. prod.), gives (1) (3) 2-chloro-1-methylantranthraquinone, yel. ndls. from AcOH, m.p. 181° (1), 180.7-181.0° (3). [Dif. from 1-chloro-2-methylbutadiene-1,3 (3:9200) q.v.]

3:7360 (1) Jacobson, Carothers, *J. Am. Chem. Soc.* 55, 1624-1627 (1933). (2) Jacobson (to du Pont), U.S. 1,950,440, March 13, 1934; *Cent.* 1934, II 1037; *C.A.* 28, 3270 (1934). (3) Sargent, Buchman, Farquhar, *J. Am. Chem. Soc.* 64, 2693 (1942).

3:7365 4-CHLORO-2-METHYLBUTANE

(Isoamyl chloride;

1-chloro-3-methylbutane)



$\text{C}_5\text{H}_{11}\text{Cl}$

Beil. I - 135

I<sub>1</sub>-(46)

I<sub>2</sub>-(100)

B.P. F.P.  
101° (1) -104.4° (6)  $D_4^{20} = 0.8027$  (7)  $n_D^{20} = 1.4096$  (7)  
100-101° (2) 0.8732 (25) 1.40909 (25)  
99.15° at 760 mm. (3) 1.4087 (6)  
99° at 777 mm. (25)  
98.8° at 760 mm. (4) (5)  
98.1° (6)

$\bar{C}$  forms many azeotropes: e.g.,  $\bar{C}$  with EtOH (1:6130), b.p. 78.3°, gives a const.-boilg. mixt., b.p. 74.8° at 760 mm., contg. 59 wt. %  $\bar{C}$  (8); with *n*-propyl alc. (1:6150), b.p. 97.2°, a const.-boilg. mixt., b.p. 89.4° at 760 mm., contg. 69 wt. %  $\bar{C}$  (8); with isopropyl alc. (1:6135), b.p. 82.45°, a const.-boilg. mixt., b.p. 79.2° at 760 mm., contg. 57 wt. %  $\bar{C}$  (8); with isobutyl alc. (1:6165), b.p. 107.85°, a const.-boilg. mixt., b.p. 94.5° at 760 mm., contg. 78 wt. %  $\bar{C}$  (8). [For still others see Beil. I<sub>2</sub>-(101).]

[For prepn. of  $\bar{C}$  from ————

HCl + ————

ZnCl<sub>2</sub> ( ————

(100% ————

[For study of hydrolysis by aq. at 80° and 180°, loss of HCl at 180°, and esterification with NaOAc at 180° see (1).]

[For study of rate of reactn. with KI in acetone at 80° see (2); for use in anal. of mixts. of  $\bar{C}$  with 1-chloro-2-methylbutane (3:7345) see (5).]

$\bar{C}$  with Mg in dry ether + trace  $I_2$  gives  $RMgCl$  (yield in 5 hrs. 96.3% (26)); this upon oxidation with  $O_2$  yields (17) isoamyl alc. (1:6200) q.v. [Note: for m.p./compn. data for mixts. of *N*-phenylcarbamates of isoamyl alc. (1:6200) and *d,l*-sec.-butylcarbinol (1:6195) see orig. ref. (17).]

⑤ Isocaproanilide: m.p. 112.0° (18) (19); 111.5° (20); 110.5° u.c. (21); 108° cor. (22). [From  $RMgCl$  (21) or  $RMgBr$  (22) with phenyl isocyanate.]

⑥ Isocapro-*p*-toluidide: m.p. 63.0° (18); 61.5–62.5° u.c. (21). [From  $RMgCl$  + *p*-tolyl isocyanate (21).]

⑦ Isocapro- $\alpha$ -naphthalide: m.p. 110–111° u.c. (21). [From  $RMgCl$  +  $\alpha$ -naphthyl isocyanate (21).]

⑧ Isoamyl mercuric chloride ( $RHgCl$ ): m.p. 86° (23).

⑨ *S*-Isoamylisothiurea picrate: m.p. 173° (24). [In poor yield from  $\bar{C}$  in alc. on refluxing 2 hrs. with thiourea, followed by addn. of  $PhOH$  (24).]

— *N*-(Isoamyl)tetrachlorophthalimide: lfts. from  $EtOH$ , m.p. 170–171° (27).

3:7365 (1) Ayres, *Ind. Eng. Chem.* 21, 900 (1929). (2) Conant, Hussey, *J. Am. Chem. Soc.* 47, 485 (1925). (3) Timmermans, *Bull. soc. chim. Belg.* 30, 66 (1921). (4) Hass, McBee, Weber, *Ind. Eng. Chem.* 27, 1192 (1938). (5) Hass, Weber, *Ind. Eng. Chem., Anal. Ed.*, 7, 231–233 (1935). (6) Turkevich, Smyth, *J. Am. Chem. Soc.* 64, 737 (1942). (7) Washburn, Keim, *J. Am. Chem. Soc.* 62, 1747 (1940). (8) Lecat, *Rec. trav. chim.* 46, 242 (1927). (9) Mouneyrat, *Ann. chim.* (7) 20, 538 (1900). (10) Malbot, *Bull. soc. chim.* (3) 1, 603 (1889).

(11) Gleditsch, *Bull. soc. chim.* (3) 35, 1094–1095 (1906). (12) Norris, Taylor, *J. Am. Chem. Soc.* 46, 756 (1924). (13) Clark, Streight, *Trans. Roy. Soc. Can.* (3) 23, III 77–89 (1929). (14) Dehn, Davis, *J. Am. Chem. Soc.* 29, 1332 (1907). (15) Cahours, *Ann.* 37, 164 (1841). (16) Ross, Bibbins, *Ind. Eng. Chem.* 31, 255–256 (1939). (17) Davydova, Papkina, Tischenko, *J. Gen. Chem. (U.S.S.R.)* 6, 1615–1623 (1936); *Cent.* 1937, I 3786. (18) Hommelen, *Bull. soc. chim. Belg.* 42, 249 (1933). (19) Brunner, Farmer, *J. Chem. Soc.* 1937, 1044. (20) Dragendorff, *Ann.* 487, 70 (1931).

(21) Underwood, Gale, *J. Am. Chem. Soc.* 56, 2119 (1934). (22) Schwartz, Johnson, *J. Am. Chem. Soc.* 53, 1005 (1931). (23) Marvel, Gauerke, Hull, *J. Am. Chem. Soc.* 47, 3010 (1925). (24) Levy, Campbell, *J. Chem. Soc.* 1939, 1443. (25) Vogel, *J. Chem. Soc.* 1943, 638, 640. (26) Houben, Boedler, Fischer, *Ber.* 69, 1769, 1782 (1936). (27) Allen, Nicholls, *J. Am. Chem. Soc.* 56, 1400–1410 (1934).

3:7370 *n*-BUTYRYL CHLORIDE  $CH_3CH_2CH_2C(=O)Cl$   $C_4H_7OCl$  Beil. II - 274  
 $\begin{array}{c} | \\ Cl \end{array}$  II<sub>1</sub>-(122)  
 II<sub>2</sub>-(251)

B.P.		F.P.		
101.8°	at 760 mm.	(1) -89.0° (12)	$D_4^{25} = 1.0154$ (2)	
102°		(2) -89.3° (1)	$n_D^{25} = 1.4115$ (2)	
101.5°	at 768 mm.	(3)	$D_4^{20} = 1.0277$ (13)	
101.4–102°		(4)	1.0205 (3)	
101.1–101.5°		(5)	$n_D^{20} = 1.4130$ (11)	
101–101.5°	at 730 mm.	(6) (7)	1.4126 (3)	
101–102.5°		(8)	1.41209 (13)	
100–101.5°		(9)	1.4117 (6) (7)	
100–101°		(10)		
100.5°	at 733 mm.	(11)		

Comml.  $\bar{C}$  may contain unsatd. and P epds. (14).

[For prepn. of  $\bar{C}$  from *n*-butyric acid (1:1035) with  $PCl_5$  (83% yield (15)), with  $PCl_5$  (yield 69–77% (16)) (9) (17) or  $PCl_5$  +  $ZnCl_2$  (77% yield (15)), with  $SOCl_2$  (yield: 97.4% (18), 90% (19), 85% (10), 80% (6) (7), 50% (15) (20), with benzoyl chloride (80–87%

yield (8) (21), with phthalyl dichloride (3:6900) (91.5% yield (22)), with benzotrichloride (3:6540) +  $\text{ZnCl}_2$  at  $70-80^\circ$  (23), or with  $\text{SnCl}_4$  in xylene (49% yield (24)) see indic. refs.; for prepn. of  $\bar{C}$  from  $\alpha$ -chloroethyl *n*-butyrate on warming with a trace of  $\text{ZnCl}_2$  see (25); for prepn. of  $\bar{C}$  from *n*-butyric acid (1:1035) by use of methyl chlorosulfonate, benzene-sulfonyl chloride, etc., see (26).]

[ $\bar{C}$  on hfg. with *n*-butyric acid (9) or with sodium *n*-butyrate yields *n*-butyric anhydride (1:1126), b.p.  $198.2^\circ$  at 760 mm. (12), f.p.  $-75.0^\circ$  (12),  $D_4^{21} = 0.9687$  (27),  $n_D^{19.73} = 1.4124$  (27),  $n_D^{18} = 1.4143$  (28).]

$\bar{C}$  with  $\text{Cl}_2$  in  $\text{CCl}_4$  gives (17) a mixt. of  $\alpha$ -,  $\beta$ - and  $\gamma$ -chloro-*n*-butyryl chlorides, some  $\alpha$ -chloro-*n*-butyric acid anhydride also being formed (29);  $\bar{C}$  with  $\text{SO}_2\text{Cl}_2$  in pres. of dibenzoyl peroxide gives (30) 15%  $\alpha$ -chloro-*n*-butyryl chloride (3.5570), 55%  $\beta$ -chloro-*n*-butyryl chloride (3.9100), and 30%  $\gamma$ -chloro-*n*-butyryl chloride (3.5970). — For study of mech. of chlorination see (31). — [For action of  $\text{PCl}_5$  on  $\bar{C}$  see (32).]

[ $\bar{C}$  with  $\text{Br}_2$  in light yields (17) (33) (14) (34)  $\alpha$ -bromo-*n*-butyryl chloride, b.p.  $151-153^\circ$  (34), and  $\beta$ -bromo-*n*-butyryl chloride.]

[ $\bar{C}$  on cat. h $\gamma$  degenation with  $\text{H}_2$  +  $\text{Pd-BaSO}_4$  cat. in ether (35) or in vapor phase (36) gives *n*-butyraldehyde (1:0130), b.p.  $74.7^\circ$ ;  $\bar{C}$  on reduction with  $\text{Na/Hg}$  or  $\text{Na}$  in moist ether yields (37) (38) (39) octeno-4-diol-4,5 di-*n*-butyrate.]

[ $\bar{C}$  added to large excess of certain  $\text{RMgX}$  cpds. in ether is in part reduced and in part undergoes normal formn. of corresp. ketone: e.g.,  $\bar{C}$  with *tert*- $\text{BuMgCl}$  gives 0% reduction and 71% ketone formn. (6) (7) (11), products include *n*-butyl *n*-butyrate, *tert*-butyl *n*-propyl ketone (2,2-dimethylhexanone-3), and *tert*-butyl-*n*-propyl-carbinyl *n*-butyrate. —  $\bar{C}$  with excess  $\text{C}_6\text{H}_5\text{MgBr}$  gives (84% yield (40)) 1,1-diphenylbutene-1 [Beil. V-648,  $V_1$  (313)].]

[ $\bar{C}$  with chlorosulfonic acid at room temp. (41) or with  $\text{AlCl}_3$  in  $\text{CHCl}_3$  followed by aq. (42) gives di-*n*-propyl ketone (butyrene) (1.5447), b.p.  $144^\circ$ . — Note, however, that  $\bar{C}$  on hfg. with  $\text{AlCl}_3$  at  $60^\circ$  without  $\text{CHCl}_3$ , then poured into aq., yields (42) (43) 2,4,6-triethylphloroglucinol [Beil. VI-1129], m.p.  $107^\circ$ .]

[ $\bar{C}$  with ethylene +  $\text{AlCl}_3$  at  $20^\circ$  gives (70% yield (44)) (45)  $\beta$ -chloromethyl *n*-propyl ketone (1-chlorohexanone-3) [Beil. I-690];  $\bar{C}$  with cyclohexene +  $\text{SnCl}_4$  yields (46) 1-cyclohexenyl *n*-propyl ketone, b.p.  $100-102^\circ$  at 8 mm.,  $D_4^{14} = 0.930$ ,  $n_D^{15} = 1.4885$  (oxime, m.p.  $67^\circ$ , semicarbazone, m.p.  $175^\circ$ ) (46);  $\bar{C}$  with cyclohexene +  $\text{AlCl}_3$  yields (47)  $\alpha$ -methylcyclopentyl *n*-propyl ketone.]

[ $\bar{C}$  with  $\text{C}_6\text{H}_6$  +  $\text{AlCl}_3$  gives (89% yield (48)) (16) phenyl *n*-propyl ketone (butyrophenone) (1.5535), b.p.  $230^\circ$ ;  $\bar{C}$  with toluene +  $\text{AlCl}_3$  gives (49) *n*-propyl *p*-tolyl ketone [Beil. VII-330, VII $_1$ -(175)], b.p.  $230^\circ$ .]

[ $\bar{C}$  with  $\text{AlCl}_3$  + phenol yields (50) (51) (20) 45%  $\alpha$ -(*n*-butyryl)phenol, b.p.  $124-126^\circ$  at 14 mm. (51),  $119^\circ$  at 9 mm. (50), m.p.  $10.5-10.6^\circ$  (50),  $8^\circ$  (51),  $D_4^{21} = 1.0683$  (50),  $n_D^{21.5} = 1.5375$  (50) (semicarbazone, m.p.  $192-193^\circ$  (50), phenylhydrazone, m.p.  $85-87^\circ$  (51)), and 30% *p*-(*n*-butyryl)phenol, b.p.  $200^\circ$  at 15 mm. (51),  $187-189^\circ$  at 9 mm. (50), m.p.  $91-91.5^\circ$  (50) (benzoate, m.p.  $107-107.5^\circ$  (50),  $106-107^\circ$  (51)); for reactn. of  $\bar{C}$  with carvacrol (1:1760) +  $\text{AlCl}_3$  in nitrobenzene see (52), similarly with thymol (1:1430) see (53).]

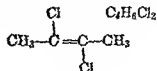
$\bar{C}$  on hydrolysis yields *n*-butyric acid (1:1035), b.p.  $164^\circ$ ; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see *n*-butyric acid (1:1035).

3:7370 (1) Timmermans, *Bull. soc. chim. Belg* 36, 507 (1927). (2) Koehl, Wenzke, *J. Am. Chem. Soc.* 59, 1418 (1937). (3) Martin, Partington, *J. Chem. Soc.* 1936, 162. (4) Reitter, *Z. physik. Chem.* 36, 137 (1901). (5) Kohlrausch, Pongratz, *Z. physik. Chem.* B-22, 381 (1933). (6) Greenwood, Whitmore, Crooks, *J. Am. Chem. Soc.* 60, 2028-2030 (1938). (7) Whitmore, *Rec. trav. chim.* 57, 565 (1938). (8) Brown, *J. Am. Chem. Soc.* 60, 1325-1328 (1938). (9)





(1939). (3) Favorskaya, *J. Gen. Chem. (U.S.S.R.)* 9, 1237-1242 (1939); *C.A.* 34, 1303 (1940).  
 (4) Hurd (to Commercial Solvents Corp.), U.S. 2,274,611, Feb. 24, 1942; *C.A.* 36, 4138 (1942).

3: 7395 *trans*-2,3-DICHLOROBUTENE-2

Beil. S.N. 11

B.P. 101-103° at 758 mm. (1)

$$D_4^{20} = 1.1416 \text{ (1)}$$

$$n_D^{19} = 1.4539 \text{ (1)}$$

$$D_4^{18} = 1.1421 \text{ (1)}$$

[See also *cis* stereoisomer (3:5500).]

[For prepn. of  $\bar{C}$  (accompanied by its *cis* stereoisomer (3:5500)) from 2,2,3-trichlorobutane (3:5630) with solid KOH (1 mole) at 135-140° see (1) ]

$\bar{C}$  on oxidn. with 3% aq.  $\text{KMnO}_4$  : : (1:1010).

$\bar{C}$  in  $\text{CCl}_4$  at -20° tr : : yields (1) acetic acid (1:1010) + acetaldehyde (1:0100).

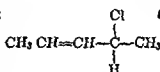
3: 7395 (1) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 6, 1553-1555 (1936); *Cent.* 1937, I 3785; *C.A.* 31, 2165 (1937).

3: 7400 *d,l*-4-CHLOROPENTENE-2

(2-Chloropentene-3;

 $\alpha,\gamma$ -dimethylallyl chloride, $\alpha$ -methylcrotyl chloride,

piperylene hydrochloride)



Beil. I - 210

I<sub>1</sub>-I<sub>2</sub>-(185)

B.P.

103° dec. at 760 mm. (1)

$$n_D^{25} = 1.4311 \text{ (5)}$$

103-106° (2)

100.5° at 771.6 mm. (3)

$$D_4^{20} = 0.9004 \text{ (3) (10)}$$

$$n_D^{20} = 1.4322 \text{ (3)}$$

68° at 270 mm. (4)

$$1.4328 \text{ (10)}$$

65° at 200 mm. (3)

57° at 200 mm. (10)

58° at 165 mm. (5)

18-20° at 12-13 mm. (1)

Two geom. stereoisomers of  $\bar{C}$  are possible but as yet unrecognized. — [A levorotatory form of  $\bar{C}$  has been obtd. (6) (7) cf. (11). —  $\bar{C}$  does not undergo allylic transposition.]

[For prepn. of  $\bar{C}$  from penten-2-ol-4 with HCl gas in the cold (3) (5), with  $\text{PCl}_5$  in dry ether (37% yield (8)) or with pyridine (4), with  $\text{PCl}_5$  (2) see indic. refs.]

$\bar{C}$  is readily hydrolyzed even by cold aq. (3); with KOH gives Sap. Eq. 106.2 (calcd. 104.6) (4). [For study of mech. of hydrolysis of  $\bar{C}$  see (4).]

[ $\bar{C}$  with HBr gives (3) 4-bromopentene-2; with phenol as specified (8) gives phenyl  $\alpha,\gamma$ -dimethylallyl ether, with diethyl sodiummalonate gives the substituted ester (5); for reactn. of  $\bar{C}$  with various aliphatic and aromatic amines see (9).]

[ $\bar{C}$  with *n*-propyl MgCl yields (10) 4-methylheptene-2, b.p. 113.5° at 760 mm.,  $D_4^{20} = 0.7206$ ,  $n_D^{20} = 1.4123$  (10).]

— *d*-( $\alpha,\gamma$ -Dimethylallyl) acetate: b.p. 136-137° (11). [From the corresp. *d*-alcohol with  $\text{Ac}_2\text{O}$  + pyridine (11).]

— *d,l*-( $\alpha,\gamma$ -Dimethylallyl) benzoate: b.p. 140° at 21 mm.;  $n_D^{20} = 1.5075$  (11). [From the corresp. *d*-alcohol with  $\text{H}_2\text{C}$  + pyridine (11).]

— *d,l*-( $\alpha,\gamma$ -Dimethylallyl) *p*-nitrobenzoate: m.p. 56° (11). [From the *d*- or *d,l*-forms of corresp. alcohol (11).]

— *d,l*-( $\alpha,\gamma$ -Dimethylallyl) *N*-( $\alpha$ -naphthyl)carbamate: m.p. 105° (11). [For important details regarding this see (11).]

3:7400 (1) Böttcher (to I.G.), *Ger.* 512,232, Nov. 7, 1930; *Cent.* 1931, I 1007; *C.A.* 25, 1037 (1931). (2) Reif, *Ber.* 41, 2711 (1908). (3) Reif, *Ber.* 41, 2711 (1908). (4) Reif, *Ber.* 41, 2711 (1908). (5) Shonle, Waldo, *J. Am. Chem. Soc.* 81, 706 (1929). (7) Hills, *Kc J. Am. Chem. Soc.* 53, 1920 (1931). *Cent.* 1929, I 3037; *C.A.* 23, 3052 (1929). (10) Henne, Chanan, Turk, *J. Am. Chem. Soc.* 63, 3474-3476 (1941).

(11) Balfe, Hills, Kenyon, Phillips, Platt, *J. Chem. Soc.* 1943, 348-351.

3:7405 ISOPROPYL CHLOROFORMATE  $C_4H_7O_2Cl$  Beil. III - 12  
(Isopropyl chlorocarbonate)  $(CH_3)_2CH.O.CO.Cl$  III<sub>1</sub>—  
III<sub>2</sub>-(10)

B.P. 103-104° (1) (2) at 723 mm. (3)

Colorless liq. insol. cold aq.

[For prepn. (40% yield (2)) from isopropyl alc. (1:6135) + phosgene (3:5000) see (2) (3); using diphosgene (3:5515) see (1).]

$\bar{C}$  on htg. with quinoline dec. at 62° (4) into isopropyl chloride (3:7025) +  $CO_2$ . [At higher temp. some propylene is also formed: for study see (5).]

Ⓐ Isopropyl carbamate [Beil. III-29]: from  $\bar{C}$  in  $C_6H_6$  by treatment with  $NH_3$  gas, filtration of pptd.  $NH_4Cl$ , and evapn. of solvent; long ndls., m.p. 92-93° (3).

Ⓐ Isopropyl *N*-phenylcarbamate (isopropyl carbanilate) [Beil. XII-321]: from  $\bar{C}$  + aniline; cryst. from pet. ether, m.p. 75-76° (6). [Previous recorded values are erroneous.]

3:7405 (1) Nekrassow, Melnikow, *J. prakt. Chem.* (2) 127, 215 (1930). (2) Hamilton, Sly, *J. Am. Chem. Soc.* 47, 436-437 (1925). (3) Thiele, *Dent. Ann.* 302, 269-270 (1898). (4) Carré, *Bull. soc. chim.* (5) 3, 1072 (1936). (5) Compere, *Proc. Louisiana Acad. Sci.* 6, 93-98 (1942); *C.A.* 36, 2779 (1942). (6) Weizmann, Garrard, *J. Chem. Soc.* 117, 328 (1920).

3:7410 5-CHLOROPENTENE-1  $Cl$   $C_5H_9Cl$  Beil. S.N. 11  
 $CH_2.CH_2.CH_2.CH=CH_2$

B.P.

103.5-104.5° at 773 mm. (1)  $D_4^{20} = 0.9125$  (1)  $n_D^{20} = 1.42973$  (1)

105° at 745 mm. (2)

36.5° at 61 mm. (1)  $D_{15}^{19} = 0.916$  (2)  $n_D^{19} = 1.43055$  (2)

Colorless limpid liq. with odor like allyl chloride but weaker; alm. insol. aq. (1).

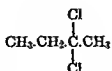
[For prepn. of  $\bar{C}$  from penten-1-ol-5 with  $PCl_3$  + pyridine (1) or with  $SOCl_2$  + dimethyl-aniline (2) see indic. refs.]

[For study of rate of reactn. of  $\bar{C}$  with  $KI$  in acetone see (1).]

— 5-Phthalimidopentene-1: m.p. 40°, b.p. 155-157° at 12 mm. (3). [Not reported from  $\bar{C}$  but obtd. in 90% yield (3) from 5-bromopentene-1 with  $K$  phthalimide in xylene at 150-160° for 6 hrs.]

3:7410 (1) Juvala, *Ber.* 63, 1994-1997 (1930). (2) Paul, *Compt. rend.* 193, 599 (1931). (3) Kharasch, Fuchs, *J. Org. Chem.* 9, 370 (1944).

## 3:7415 2,2-DICHLOROBUTANE

 $\text{C}_4\text{H}_8\text{Cl}_2$ 

Beil. I - 119

 $\begin{array}{l} \text{I}_1- \\ \text{I}_2- \end{array}$ 

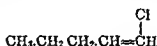
B.P.		M.P.			
104-104.5°	(1)	-74° (3)	$D_4^{20} = 1.0665$	(2)	$n_D^{20} = 1.4306$ (2)
102-104°	(2) (3)				
99-102° at 760 mm.	(4) (5)		$D_4^{21.8} = 1.069$	(5)	$n_D^{22} = 1.4270$ (4)

[For prepn. from butanone (ethyl methyl ketone) (1:5405) with  $\text{PCl}_5$  see (8) (5) (4) (6) (1); for formn. (together with other isomers and 2-chlorobutene-1 (1)) from 2-chlorobutane (3:7125) by chlorination see (2).]

$\bar{\text{C}}$  with alc. KOH splits off HCl and gives mixt. of both stereoisomeric 2-chlorobutene-2's (2) (9) (3:7105). [Cleavage of HCl in the other sense to yield mainly 2-chlorobutene-1 (3:7075) is also claimed (7).]

Ber. 8, 412 (1875). (7) Schjaneberg, Ber. 71, 573 (1938). (8) Henne, Renoll, Leicester, J. Am. Chem. Soc. 61, 940 (1939). (9) Charpentier, Bull. soc. chim. (5) 3, 1407-1411 (1934).

## 3:7420 1-CHLOROPENTENE-1

 $\text{C}_5\text{H}_9\text{Cl}$ 

Beil. S.N. 11

B.P. 102-100° (1)

Two geom. stereoisomers of  $\bar{\text{C}}$  are possible but as yet unrecognized.

[For prepn. of  $\bar{\text{C}}$  from 1,2-dichloropentane (3:8140) with alc. KOH see (1).]

3:7420 (1) Lemke, Tishchenko, J. Gen. Chem. (U.S.S.R.) 7, 1995-1998 (1937); Cent. 1939, I 2398; C.A. 32, 482 (1938)

## 3:7425 1,1-DICHLORO-2-METHYLPROPANE

(Isobutyridene (di)chloride)

 $\text{C}_4\text{H}_7\text{Cl}_2$ 

Beil. I - 126

 $\begin{array}{l} \text{I}_1- \\ \text{I}_2- \end{array}$ 

B.P. 105-106°	(1)	$D_{12}^{12} = 1.0111$	(5)
104.3-105.7°	(2)		
108°	(3)		
103-105°	(5)		

Colorless liq. with agreeable odor.

[For prepn. from isobutyraldehyde (1:0120) +  $\text{PCl}_5$  see (5) (2); for formn. (with other products) during chlorination of isobutane see (1) (3).]

$\bar{\text{C}}$  htd. in s.t. with  $\text{Ag}_2\text{O}$  +  $\text{H}_2\text{O}$  yields Ag isobutyrate (4).

3:7425 (1) Hass, McBee, Weber, Ind. Eng. Chem. 27, 1191 (1935). (2) Kohlrausch, Köppl. Monatsh. 65, 197 (1935). (3) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,072, June 4, 1935; Cent. 1936, I 3012. (4) Spring, Lecrenier, Bull. soc. chim. (2) 48, 626 (1887). (5) Oeconomides, Bull. soc. chim. (2) 45, 497-498 (1851).

3:7430 1,2-DICHLORO-2-METHYLPROPANE  $\text{CH}_3 \cdot \text{C}_4\text{H}_8\text{Cl}_2$  Beil. I - 120  
 (Isobutylene dieldride)  $\text{CH}_3-\text{C}-\text{CH}_2$  I<sub>1</sub>-(41)  
 $\text{Cl} \quad \text{Cl}$  I<sub>2</sub>-(88)

B.P. 100.5° cor. at 760 mm. (1)  
 107-108° (3) (4) (5) (6) (7)  
 59-60° at 150 mm. (1)  
 38.0-30.2° at 70 mm. (1)

$D_4^{20} = 1.089$  (4)  $n_D^{20} = 1.4370$  (1)  
 $D_{20}^{20} = 1.093$  (1).  $n_D^{17} = 1.4373$  (3)

Liq. with mild clean sweetish odor; stable on stdg. and develops no HCl even in 6 months (1).

[For prepn. from *ter*-butyl chloride (3:7015) by chlorination see (1) (2) (8); from 2-methylpropene (isobutylene) by addn. of  $\text{Cl}_2$  at 0° see (4); from 1-chloro-2-methylpropanol-2 (3:7752) with conc. HCl see (2) (9); from isobutane by chlorination see (10).]

Upon hydrolysis the tertiary chlorine atom shows great reactivity, the primary chlorine atom little. Thus  $\bar{\text{C}}$  on boiling with aq. for 18 hrs. gives (48% yield (2)) 1-chloro-2-methylpropanol-2 (3:7752). [The addn. of bases ( $\text{NaOH}$  or  $\text{NaHCO}_3$ ) or antiaids ( $\text{CaCO}_3$ ) results in lower yields (2).] [In addn. to the above 1-chloro-2-methylpropanol-2 the presence of  $\text{NaHCO}_3$  or  $\text{Na}_2\text{CO}_3$  leads (11) to formn. of 2-methylpropanediol-1,2 (isobutylene glycol) [Beil. I-480], 1-chloro-2-methylpropene-1 ("isocrotyl chloride") (3:7120), and isobutyraldehyde (1:0120).] [For study of methods of conversion of  $\bar{\text{C}}$  to isobutyraldehyde see (1).]

3:7430 (1) Hersh, Nelson, *Chem. Soc.* 58, 1010-1011  
 (4) Burgin, Engs, Groll, 1  
*Ind. Eng. Chem.* 27, 119  
 Pogorshelski, *J. Russ. Ph.*  
 Nelson, *J. Am. Chem. Sc.*  
 (10) Haas, McBeo (to Pu  
 I 3012. ks, Nelson, *J. Am.*  
 1. B-48, 10 (1011).  
 s, McBeo, Weber,  
 -534 (1900). (7)  
 068, (8) Rogers,  
 . 142, 408 (1900).  
 1035; *Cent.* 1936,

(11) Dobryanskii, Gutner, Shchigel'skaya, *J. Gen. Chem. (U.S.S.R.)* 7, 1315-1320 (1937); *Cent.* 1038, I 501; *C.A.* 31, 0189 (1937).

3:7450  $\alpha,\alpha$ -DIMETHYLPROPIONYL CHLORIDE  $\text{C}_3\text{H}_7\text{OCl}$  Beil. II - 320  
 (Trimethylacetyl chloride;  
 pivalyl chloride)  $\text{CH}_3-\text{C}-\text{C}=\text{O}$  II<sub>1</sub>-(139)  
 $\text{CH}_3 \quad \text{Cl}$  II<sub>2</sub>-(280)

B.P.		B.P.		
107°	(1)	70.5°-71.0° at 250 mm. (5) (6)		$n_D^{20} = 1.4126$ (7)
105-106°	(2)	58° at 150 mm. (7)		1.4125 (9)
104.3-105.4°	(3)	57.0° at 150 mm. (8)		1.4123 (9)
103-104°	(4)	56° at 150 mm. (9)		1.4122 (8)
		48° at 100 mm. (9)		1.4118 (5) (6)

[For prepn. of  $\bar{\text{C}}$  from trimethylacetic acid (pivalic acid) (1:0410) with  $\text{PCl}_5$  (2), with  $\text{PCl}_3$  (10), with  $\text{SOCl}_2$  (11) (yield 86% (5) (6) (8), 86% (7)), or with benzoyl chloride (1 mole 79% yield, 2 moles 92% yield (4) cf. (10)) see indic. refs.; for formn. of  $\bar{\text{C}}$  (together with other prods.) from isobutane +  $\text{CO}$  +  $\text{AlCl}_3$  at 20° and 120 atm. see (12).]

[ $\bar{\text{C}}$  with MeOH gives (50% yield (8)) methyl trimethylacetate (1:3072), b.p. 99.5° at

731 mm.,  $n_D^{20} = 1.3895$  (8);  $\bar{C}$  with sodium trimethylacetate yields (2) pivalic anhydride, b.p.  $124^\circ$  at 93 mm.,  $n_D^{20} = 1.4033$  (6).]

[ $\bar{C}$  with large excess of most Grignard reagents is reduced to *ter*-butyl carbinol (neopentyl alcohol) (1:5812), other products also being formed; for reactn. of  $\bar{C}$  with  $\text{EtMgBr}$  (8) (13), with *n*- $\text{PrMgBr}$  (13), with *iso*- $\text{PrMgBr}$  (13), with *n*- $\text{BuMgBr}$  (5) (7) (13), with *iso*- $\text{BuMgBr}$  (13) or *iso*- $\text{BuMgI}$  (9), with *ter*- $\text{BuMgCl}$  (5) (6) (9), with *n*- $\text{AmMgBr}$  (13), with *iso*- $\text{AmMgBr}$  (13), with *ter*- $\text{AmMgCl}$  (9), with neopentyl  $\text{MgCl}$  (9) see indic. refs.]

[For study of rate of reactn. of  $\bar{C}$  with various aces. see (14).]

$\bar{C}$  on hydrolysis yields trimethylacetic acid (1:0410) q.v. (for the amide, m.p.  $132.0$ – $132.6^\circ$  cor. (15), anilide, m.p.  $132^\circ$  cor. (16), *p*-toluidide, m.p.  $119.5^\circ$  cor. (16), and other derivatives (16) corresp. to  $\bar{C}$  see 1:0410 and indic. refs.).

3:7450 (1) Böeseken, *Rec. trav. chim.* 29, 99 (1910). (2) Butlerow, *Ann.* 173, 373–374 (1874). (3) Kohlrausch, Pongratz, *Z. physik. Chem.* B-22, 382 (1933). (4) Brown, *J. Am. Chem. Soc.* 60, 1325–1328 (1938). (5) Whitmore, *Rec. trav. chim.* 57, 562–568 (1938). (6) Greenwood, Whitmore, Crooks, *J. Am. Chem. Soc.* 60, 2028–2030 (1938). (7) Whitmore, Popkin, Whitaker, Mattil, Zech, *J. Am. Chem. Soc.* 60, 2458–2462 (1938). (8) Whitmore, Foster, *J. Am. Chem. Soc.* 64, 2966–2968 (1942). (9) Whitmore, Whitaker, Mosher, Breivik, Wheeler, Miner, Sutherland, Wagner, Clapper, Lewis, Lux, Popkin, *J. Am. Chem. Soc.* 63, 643–654 (1941). (10) Whit-

more, *Ber.* 69,

–2789 (1938).

*n. Chem. Soc.*

67, 1785 (1945). (16) Degnan, Shoemaker, *J. Am. Chem. Soc.* 68, 105 (1946).

### 3:7455 5-CHLOROPENTENE-2

 $\text{C}_5\text{H}_9\text{Cl}$ 

Beil. S.N. 11

(1-Chloropentene-3)

 $\text{CH}_3\text{CH}=\text{CH}.\text{CH}_2\text{CH}_2\text{Cl}$ 

B.P.

 $107.0$ – $107.6^\circ$  at 755 mm. (1)

 $D_4^{20} = 0.9943$  (1)  $n_D^{20} = 1.4310$  (1)

Two geom. stereoisomers of  $\bar{C}$  are possible but as yet unrecognized.

[For prepn. of  $\bar{C}$  in 75% yield from penten-3-ol-1 with  $\text{SOCl}_2$  in  $\text{CH}_2\text{Cl}_2$  see (1).]

$\bar{C}$  with  $\text{NaI}$  in acetone gives (1) after 11 hrs. reflux 74% yield 1-iodopentene-3, b.p.  $53.6^\circ$  at 20 mm.,  $D_4^{20} = 1.5579$ ,  $n_D^{20} = 1.5153$  (1).

$\bar{C}$  with  $\text{Mg}$  in dry ether yields  $\text{RMgCl}$  (used in reactn. with acrolein (1:0115) to give (50% yield (1)) penten-3-yl-vinyl-carbinol).

3:7455 (1) Goethals, *Bull. soc. chim. Belg.* 46, 417–419 (1937).

### 3:7460 1-CHLOROPENTANE

 $\text{C}_5\text{H}_{11}\text{Cl}$ 

Beil. I - 130

 (*n*-Amyl chloride,

 $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{Cl}$ 
*n*-butylcarbonyl chloride)

 $I_1$ -( 42)

 $I_2$ -( 95)

B.P.

F.P.

 $108.35^\circ$  cor. at 760 mm. (1) (2)  $-99^\circ$  (2)  $D_4^{25} = 0.87667$  (2)

 $107.74$ – $107.78^\circ$  at 760 mm. (3)  $n_D^{25} = 1.41026$  (2)

 $107$ – $108^\circ$  (4)  $D_4^{20} = 0.8828$  (8)

 $105.7$ – $105.8^\circ$  at 769.3 mm. (5)  $0.8821$  (30)

 $105^\circ$  at 764 mm. (30)  $0.8816$  (2)

 $107.8$ – $108.4^\circ$  at 749.7 mm. (6)  $n_D^{20} = 1.41280$  (8)

 $106.6^\circ$  at 739.8 mm. (7)  $1.41253$  (2)

 $106^\circ$  at 725 mm. (8)  $1.41177$  (30)

 $D_4^{15} = 0.88657$  (2)

 $n_D^{15} = 1.41481$  (2)

Note that most samples of  $\bar{C}$  reported prior to 1938 undoubtedly contained a small amount of mixed 2-chloropentane (3:7325) and 3-chloropentane (3:7330). This previously unrecognized fact may be the cause of much variation in reported physical constants, especially the refractive index.

[For prepn. of  $\bar{C}$  (or its mixt. with 2-chloro- and 3-chloropentane) from pentanol-1 (1:6205) with conc. HCl (7) (4) in s.t. nt 120° for 12–15 hrs. (94% yield (2)) see indic. refs.; with HCl + ZnCl<sub>2</sub> (yield: 67% (30), 57% (8), 72% (9)) see (8) (9) (30); with PCl<sub>3</sub> + ZnCl<sub>2</sub> (70% yield (9)) or PCl<sub>3</sub> + ZnCl<sub>2</sub> (76% yield (9)) see (9); with SOCl<sub>2</sub> + pyridine (gives no rearrangement (8)) (yield: 80% (8), 87% (9)) see (8) (9); for prepn. (23% yield (10)) from  $\gamma$ -chloropropyl *p*-toluenesulfonate by reactn. with EtMgBr see (10).]

[For formn. of  $\bar{C}$  (together with other products) during chlorination of pentane see (11) (12) (13) (14).]

$\bar{C}$  with EtOH forms const.-boilg. mixt., b.p. 72.5°, but forms no azeotrope with MeOH.  $\bar{C}$  forms with aq. a const.-boilg. mixt., b.p. 82°.

$\bar{C}$  on htg. with conc. HCl + ZnCl<sub>2</sub> at 126–134° for 12 hrs. undergoes partial isomerization forming 3% of a mixt. of 2-chloropentane (3:7325) and 3-chloropentane (3:7330) (8).

[For study of rate of hydrolysis by aq. at 80° and 180°, and rate of cleavage of HCl at 180°, see (11); for rate of reactn. with KI in acetone see (4) (15) (16); for reactn. with Na—C $\equiv$ CH see (17) (18); with KCN see (19); with Cl<sub>2</sub> see (6); for extensive study of reactn. with Na see (19) (20) (21) (22) (23) (24) (25).]

④ *n*-Caproanilide:  $\bar{C}$  with Mg in dry ether yields RMgCl which upon reactn. with phenyl isocyanate and subsequent hydrolysis yields (26) *n*-caproanilide, m.p. 96° cor. (27), 94–95° u.c. (20), 92° (23).

⑤ *n*-Capro-*p*-toluidide: m.p. 74–75° u.c. (26), 73° (28). [From RMgCl + *p*-tolyl isocyanate as above (26).]

⑥ *S*-*n*-Amylthiourea picrate: m.p. 154° (29). [From  $\bar{C}$  in alc. on refluxing 2 hrs. with thiourea, followed by addn. of PkOH (29).]

— *N*-(*n*-Amyl)tetrachlorophthalimide: ndls. from CHCl<sub>3</sub>, poured into 2 vols. MeOH, m.p. 145–146° (31).

3:7460 (1) Hass, *J. Chem. Education* 13, 492–493 (1936). (2) Simon, *Bull. soc. chim. Belg.* 33, 48, 50, 58 (1929). (3) Rintelen, Saylor, Gross, *J. Am. Chem. Soc.* 59, 1129 (1937). (4) Conant, Kirner, *J. Am. Chem. Soc.* 46, 245 (1924). (5) Karvonen, *Ann. Acad. Sci. Fennicae* 3-A, 1–103; *Cent.* 1912, II 1271. (6) Hass, Huffman, *J. Am. Chem. Soc.* 63, 1233–1235 (1941). (7) Lieben, Rossi, *Ann.* 159, 72 (1871). (8) Whitmore, Karnatz, Popkin, *J. Am. Chem. Soc.* 60, 2540–2542 (1938). (9) Clark, Streight, *Trans. Roy. Soc. Can.* (3) 23, III 77–89 (1929). (10) Rossander, Marvel, *J. Am. Chem. Soc.* 50, 1495 (1928).

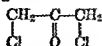
(11) Ayres, *Ind. Eng. Chem.* 21, 899–904 (1929). (12) Clark, *Ind. Eng. Chem.* 22, 439–443 (1930). (13) Ayres (to B.A.S. Co.), U.S. 1,741,393, Dec. 31, 1929; *Cent.* 1930, I 3353. (14) Sharples Solv. Corp., Ger. 610,660, March 18, 1935; *Cent.* 1935, II 020. (15) Conant, Hussey, *J. Am. Chem. Soc.* 47, 485 (1925). (16) Conant, Kirner, Hussey, *J. Am. Chem. Soc.* 47, 587–589 (1925). (17) Hurd, Christ, *J. Org. Chem.* 1, 143–144 (1936). (18) Vaughn, Hennion, Vogt, Nieuwland, *J. Org. Chem.* 2, 1–22 (1937). (19) Hass, Marshall, *Ind. Eng. Chem.* 23, 352–353 (1931). (20) Morton, LeFevre, Hechenbleikner, *J. Am. Chem. Soc.* 58, 757 (1936).

(21) Morton, Hechenbleikner, *J. Am. Chem. Soc.* 58, 1700 (1936). (22) Morton, Hechenbleikner, *J. Am. Chem. Soc.* 58, 2599–2605 (1936). (23) Morton, Richardson, *J. Am. Chem. Soc.* 62, 123–126 (1940). (24) Morton, Richardson, *J. Am. Chem. Soc.* 62, 129–131 (1940). (25) Gilman, Pacevitz, *J. Am. Chem. Soc.* 62, 1301–1302 (1940). (26) Underwood, Gale, *J. Am. Chem. Soc.* 56, 2119 (1934). (27) Schwartz, Johnson, *J. Am. Chem. Soc.* 53, 1065 (1931). (28) Robertson, *J. Chem. Soc.* 115, 1220–1221 (1910). (29) Levy, Campbell, *J. Chem. Soc.* 1939, 1443. (30) Vogel, *J. Chem. Soc.* 1943, 638, 640.

(31) Allen, Nicholls, *J. Am. Chem. Soc.* 56, 1409–1410 (1934).

## 3:0563 1,3-DICHLOROPROPANONE-2

( $\alpha,\alpha'$ -Dichloroacetone,  
*sym.*-dichloroacetone,  
*bis*-(chloromethyl) ketone)

 $\text{C}_3\text{H}_4\text{OCl}_2$ 

Boil. I - 655

I<sub>1</sub>-(344)I<sub>2</sub>-(719)

M.P.		B.P.	
45°	(1) (2)	173.0-173.4° cor. at 759 mm. (4)	$D_4^{20} = 1.3843$ (4)
44°	(16)	172.6-173.0° cor. at 748 mm. (4)	1.3809 (4)
43-44°	(3) (8)	172.3-172.8° cor.	(1)
43°	(4) (10)	172-173°	(3) $n_D^{20} = 1.47223$ (4)
42.5-43°	(7)	172°	(2) (9) (20) 1.47144 (4)
42.5°	(5) (20)	170-171°	(6)
42-43°	(4) (22)	170°	(8)
		168-169°	at 723 mm. (7)

Colorless tils. or ndls. volatile even at ord. temp. — Vapors are lachrymatory; liquid blisters skin. — Appreciably sol. in aq. especially on warming, eas. sol. alc., ether. — Volatile with steam.

[For prepn. of  $\bar{C}$  from 1,3-dichloropropanol-2 (glycerol  $\alpha$ -dichlorohydrin) (3:5985) by oxidn. with  $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$  (68-75% yield (10)), with  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$  (1) (2) (4) (6) (7) (8) (9) (11) (generally poorer yields) see indic. refs (note also that h.p. of  $\bar{C}$  is very close to that of the precursor 1,3-dichloropropanol-2 (3:5985), a fact which leads to some doubt as to the true yield of  $\bar{C}$  in certain of the older reports); for prepn. of  $\bar{C}$  from acetone (1:5400) with  $\text{Cl}_2$  directly (12), in pres. of  $\text{I}_2$ ,  $\text{FeCl}_3$ , or  $\text{SbCl}_5$  (yield: 28%  $\bar{C}$  accompanied by 48.6% *unsym.*-dichloroacetone (3:5430) (13)), in pres. of  $\text{NiCl}_2$  at 70° (other prods. are also formed (14)), or in pres. of aq. +  $\text{CaCO}_3$  (yield: 10%  $\bar{C}$  accompanied by other prods. (16)) (4) (15), see indic. refs.]

[For prepn. of  $\bar{C}$  from epichlorohydrin (3-chloro-1,2-epoxypropane) (3:5353) with  $\text{S}_2\text{Cl}_2$  (yield: 33%  $\bar{C}$  accompanied by 67% 1,3-dichloropropanol-2 (3:5985) (17)), from ethyl  $\gamma$ -( $\alpha$ )-chloro- $\alpha$ -( $\gamma$ )-ethoxyacetate (18) or from ethyl  $\alpha,\gamma$ -dichloroacetate (19) by ketonic cleavage with  $\text{HCl}$ , from allene (propadiene) (20) or 1,2-dichloropropene-2 (21) with  $\text{HOCl}$ , or from 1,3-dihydroacetone on digestion with  $\text{AgCl}$  (22) cf. (3) see indic. refs.]

[ $\bar{C}$  on reduction with yeast gives (53% yield (2)) 1,3-dichloropropanol-2 (3:5985), b.p. 178° (2). —  $\bar{C}$  with  $\text{Zn} + \text{AcOH}$  does not give acetone but yields (23) a gas formerly supposed to have been cyclopropanone (since it yielded with semicarbazide a semicarbazone, m.p. 156° (23)) although in the light of later work (21) (25) (26) this now appears very doubtful. — For polarographic study of reduction potential of  $\bar{C}$  see (27).]

$\bar{C}$  with aq. alk. presumably yields 3-chloropropanone-2-ol-1 [Boil. I-823] and/or propenone-2-ol-1,3 (dihydroxyacetone) [Boil. I-816, I<sub>1</sub>-(428), I<sub>2</sub>-(689)] since  $\bar{C}$  readily reduces Fehling's soln. (28).

$\bar{C}$  with satd. aq.  $\text{NaHSO}_3$  soln. yields a  $\text{NaHSO}_3$  cpd. which seps. with  $2\frac{1}{2} \text{H}_2\text{O}$  (1),  $3 \text{H}_2\text{O}$  (7). —  $\bar{C}$  with aq.  $\text{K}_2\text{SO}_3$  soln. yields (30) corresp. salt of acetone- $\alpha,\alpha'$ -disulfonic acid [Boil. IV<sub>2</sub>-(530)].

[ $\bar{C}$  with  $\text{KOAc}$  (slightly more than 1 mole) in boilg.  $\text{AcOH}$  gives (48% yield (29)) chloroacetyl methyl acetate, b.p. 112-114° at 16 mm. (29) —  $\bar{C}$  with  $\text{K}$  benzoate refluxed in alc. yields (23) 1,3-dibenzoyloxyacetone, long ndls. from alc., but m.p. not reported.]

[ $\bar{C}$  in dry  $\text{MeOH}$  treated with  $\text{HCl}$  gas gives (81.5% yield (31)) 1,3-dichloroacetone dimethylketal, cryt. from  $\text{MeOH}$ , m.p. 81.5° (31);  $\bar{C}$  in abs.  $\text{EtOH}$  similarly treated gives (smaller yield (31)) 1,3-dichloroacetone diethylketal, m.p. 28° (31). — For reactn. of  $\bar{C}$  with ethylene glycol see (32).]



[For prepn. of  $\bar{C}$  from  $\beta,\beta'$ -dichlorodiethyl ether (3:6025) with solid  $N_2OH$  at  $200^\circ$  (1) or with triethanolamine + solid  $NaOH$  (70% yield (2)) see indic. refs.]

$\bar{C}$  is stable toward alkalis but with dil. acids even in cold is readily and quant. hydrolyzed (1) to  $\beta$ -chloroethanol (3:5552) and acetaldehyde (1:0100).

$\bar{C}$  with diethyl sodiomalonate gives (73% yield (1)) diethyl  $\beta$ -(vinylxy)ethyl malonate, b.p.  $130-135^\circ$  at 0 mm.,  $D_{15}^{20} = 1.0575$  (1); this prod. condenses (1) with urea to give 5-( $\beta$ -(vinylxy)ethyl)barbituric acid (whose properties appear to be subsequently unreported) which itself with dil. minl. acid hydrolyzes to give 5-( $\beta$ -hydroxyethyl)barbituric acid, m.p. above  $300^\circ$  (3). — For analogous reactions of  $\bar{C}$  with various diethyl alkylmalonates and reaction of the products with urea to give the corresp. 5-alkyl-5-( $\beta$ -(vinylxy)ethyl)-barbituric acids see (3). —  $\bar{C}$  with diethyl phenyl-sodio-malonate in s.t. at  $140-145^\circ$  for 14 hrs. gives (52% yield (4)) diethyl 5-phenyl-5-( $\beta$ -(vinylxy)ethyl)malonate, b.p.  $196-197^\circ$  at 17 mm.,  $D_4^{20} = 1.098$ ; this prod. with urea gives (4), 5-phenyl-5-( $\beta$ -(vinylxy)ethyl)-barbituric acid which upon hydrolysis with dil. acid gives (10% yield (4)) 5-phenyl-5-( $\beta$ -hydroxyethyl)barbituric acid ("hydroxyluminal").]

$\bar{C}$  with phenylacetonitrile gives (50% yield (4)) phenyl-( $\beta$ -vinylxyethyl)acetonitrile, b.p.  $147^\circ$  at 8 mm.,  $D_4^{20} = 1.029$  (4).]

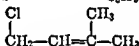
[For use of  $\bar{C}$  in prepn. of cellulose ethers see (5).]

1176 (1925). (2) Chitwood, 4, 1938; *Cent.* 1938, I 4236; 4238; *C.A.* 32, 1278 (1938). 925). (4) Nelson, Cretcher, *ibid.*, U.S. 2,082,797, June 8,

### 3:7465 4-CHLORO-2-METHYLBUTENE-2

( $\gamma,\gamma$ -Dimethylallyl chloride;  
isoprene hydrochloride)

$C_5H_9Cl$  Beil. I - 214  
I<sub>1</sub> - (88)  
I<sub>2</sub> - (191)



B.P.  $109^\circ$  (1)

$D_4^{20} = 0.9336$  (1)  $n_D^{20} = 1.43975$  (4)

$30-33^\circ$  at 40 mm. (4)

Colorless liq. with odor like allyl chloride. —  $\bar{C}$  darkens on stdg. and loses  $HCl$  on distn. (1).

[For prepn. of  $\bar{C}$  from 2-methylbutadiene-1,3 (isoprene) (1:8020) by 1,4-addn. of dry  $HCl$  gas see (1) (4).]

$\bar{C}$  on htg. in s.t. with  $KOAe$  +  $AcOH$  (1) or passed over  $TiO_2$  at  $425-450^\circ$  at reduced press. (3) loses  $HCl$  yielding isoprene (1:8020), b.p.  $34^\circ$ .

$\bar{C}$  reduces alk.  $KMnO_4$  (1).

$\bar{C}$  in conc.  $HCl$  satd. with  $HCl$  gas gives (94% yield (1)) 2,4-dichloro-2-methylbutane (3:8105), b.p.  $145-146^\circ$  (1) cf. (4).

$\bar{C}$  in  $CHCl_3$  adds 1  $Br_2$ , yields (1) 2,3-dibromo-4-chloro-2-methylbutane, oil decomposing on distn. even under reduced press. (1).

[For behavior of  $\bar{C}$  with  $AlCl_3$  see (2).]

3:7465 (1) Aschan, *Ber.* 51, 1303-1307 (1918). (2) Thomas, Carmody, *J. Am. Chem. Soc.* 55, 3855 (1933). (3) Müller-Cunradi (to I.G.), *Ger.* 665,160, Nov. 26, 1932. (4) Soday (to United Gas Improvement Co.), U.S. 2,376,390, May 22, 1945; *C.A.* 39, 3548 (1945).

3:7463 $\beta$ -CHLOROETHYL ETHYL ETHER	$C_4H_9OCl$	Beil. I - 337
( $\beta$ -ethoxyethyl chloride)	$CH_2O.CH_2CH_3$	$I_1$ -(170)
	$ $	$I_2$ —
	$CH_2Cl$	

B.P.			
108-109°	(1)	$D_4^{20} = 0.9945$ (5)	$n_D^{20} = 1.412$ (5)
107-108°	(2)	0.98945 (4)	1.41134 (4)
107-108°	(3)	0.98841 (7)	
107.0-107.3° at 761.8 mm.	(4) (7)		
105-107°	(5)	$D_4^{25} = 1.003$ (5)	
106° u.c. at 728 mm.	(6)		

[For prepn. of  $\bar{C}$  from  $\beta$ -ethoxyethyl alc. ("Cellosolve") (1:6410) with  $PCl_3$  (7) (8) or with  $SOCl_2$  + pyridine (20% yield (10)) (11) in  $CHCl_3$  (58.3% yield (9)) see indic. refs.; from ethylene chlorohydrin (3:5552) + ethyl alc. (1:6130) + conc.  $H_2SO_4$  at 145° see (1); from ethylene with ethyl hypochlorite (3:7022) (12) or with mixtures yielding the latter, such as  $EtOH + Cl_2$  (55% yield  $\bar{C}$  (2)) or alc.  $N,N$ -dichlorobenzene sulfonamide (5), see indic. refs.; from  $\beta$ -iodoethyl ethyl ether with  $Cl_2$ ,  $SbCl_5$ , or  $ICl$  see (3).]

$\bar{C}$  with  $NaI$  in acetone refluxed 15 hrs. gives (10) (11)  $\beta$ -ethoxyethyl iodide, b.p. 151-154° (10) (11).

[ $\bar{C}$  with  $KSH$  in a.t. at 65° for 24 hrs. (1) cf. (13) gives (74% yield (1))  $\beta$ -ethoxyethyl mercaptan, b.p. 125.5-125.8° u.c.,  $D_{20}^{20} = 0.9479$  (1) (corresp.  $EtOCH_2CH_2SH \cdot Cl$ , m.p. 152.0-153.5° dec. (1)) accompanied by (13% yield (1)) of bis-( $\beta$ -ethoxyethyl) sulfide, b.p. 220° cor., also obtd. (51% yield (1)) from  $\bar{C}$  + alc.  $Na_2S$ .]

[ $\bar{C}$  with excess  $NaOC_2H_5$  in alc. htd. 10 days gives (1)  $\beta$ -phenoxyethyl ethyl ether ( $\beta$ -ethoxyphenetole), b.p. 230°. —  $\bar{C}$  with disodium salt of hydroquinone (1:1500) gives (14) hydroquinone bis-( $\beta$ -ethoxyethyl ether), m.p. 34-35°, b.p. 210-212° at 25 mm. (14).]

[ $\bar{C}$  with diethyl malonate + alc.  $NaOEt$  gives (14% yield (1)) cf. (15) diethyl  $\beta$ -ethoxyethylmalonate, b.p. 134-138° at 15 mm. (1), 118-119° at 6 mm. (15);  $D_4^{20} = 1.0199$  (15).]

[ $\bar{C}$  with aniline refluxed 2 hrs. gives (1)  $N$ -( $\beta$ -ethoxyethyl)aniline, b.p. 262-263° cor.]

[For reactn. of  $\bar{C}$  +  $NaNH_2$  with  $\alpha$ -picoline, with  $\gamma$ -picoline, and with  $\beta$ -collidine see (16).]

3:7463 (1) Swallen, Boord, *J. Am. Chem. Soc.* 52, 653-659 (1930). (2) Ernst (to A. Wacker Soc. Elektrochem. Ind.), Ger. 537,696, Nov. 5, 1931, *Cent.* 1932, I 1153, C.A. 26, 1297 (1932). (3) Henry, *Bull. soc. chim.* (2) 44, 459 (1885); *Compt. rend.* 100, 1007 (1885). (4) Karvonen, *Ann. Acad. Sci. Fennicae* 5-A, 1-139 (1914), *Cent.* 1919, II 807, C.A. 14, 2176 (1920). (5) Shlyarov, *J. Gen. Chem. (U.S.S.R.)* 9, 2121-2125 (1939); *Cent.* 1940, II 199-200, C.A. 34, 4055 (1940). (6) Mohler, Sorge, *Helv. Chim. Acta* 23, 1208 (1940). (7) Karvonen, *Ann. Acad. Sci. Fennicae* 3-A, No. 7, 1-103 (1912); *Cent.* 1912, II 1270. (8) Chalmers, *Can. J. Research* 7, 464-471 (1932); *Cent.* 1933, I 1759; C.A. 27, 701 (1933). (9) Hurd, Fowler, *J. Am. Chem. Soc.* 61, 251 (1939). (10) Smith, Ungnade, Austin, Prichard, Opie, *J. Org. Chem.* 4, 339 (1939).

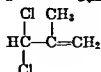
(11) Dutta, *J. Indian Chem. Soc.* 17, 652 (1940). (12) Suknevich, Chalingaryan, *J. Gen. Chem.* 2, 783-789 (1932); *Cent.* 1933, II 1170, C.A. 27, 2670 (1933). (13) Rojahn, Lemme, *Arch. Pharm.* 263, 623 (1925). (14) Sexton (to Imperial Chem. Ind., Ltd.), U.S. 2,056,299, Oct. 6, 1936; *Cent.* 1937, I 1798; C.A. 30, 8641 (1936). (15) Palomaa, Kenetti, *Ber.* 64, 800-801 (1931). (16) Chichibabine, *Bull. soc. chim.* (5) 5, 439-441 (1935).

3:7464 $\beta$ -CHLOROETHYL VINYL ETHER	$C_4H_7OCl$	Beil. I —
	$CH_2=CH_2-O-CH_2CH_2$	$I_1$ —
	$ $	$I_2$ -(473)
	$Cl$	

B.P.		
109° cor. at 740 mm.	(1)	$D_{15}^{15} = 1.0525$ (1)

3:7475 (1) Whitmore, Bernstein, Mixon, *J. Am. Chem. Soc.* **60**, 2539 (1938). (2) Whitmore, Rothrock, *J. Am. Chem. Soc.* **55**, 1105-1109 (1933). (3) Whitmore, Bernstein, *J. Am. Chem. Soc.* **60**, 2627 (1938).

3:7480 3,3-DICHLORO-2-METHYLPROPENE-1  $\text{C}_3\text{H}_4\text{Cl}_2$  Beil. S.N. 11  
(1,1-Dichloro-2-methylpropene-2)



B.P.

108-112° at 762 mm. (1)

$D_4^{25} = 1.1363$  (1)  $n_D^{25} = 1.4523$  (1)

49-50° at 120 mm. (1)

Note.  $\bar{\text{C}}$  by virtue of allylic transposition may yield derivatives of its synionic isomer 1,3-dichloro-2-methylpropene-1 (3:5590) q.v.

[For prepn. of  $\bar{\text{C}}$  (68% yield together with 32% yield of 1,1,2-trichloro-2-methylpropane (3:5710)) from 1-chloro-2-methylpropene-1 ( $\beta,\beta$ -dimethylvinyl chloride) (3:7120) with  $\text{Cl}_2$  (1 mole) +  $\text{NaHCO}_3$  (1.5 moles) at 0° see (1).]

$\bar{\text{C}}$  on htg. under reflux gives (by allylic transposition) 1,3-dichloro-2-methylpropene-1 (3:5590), b.p. 132°.

$\bar{\text{C}}$  with  $\text{O}_3$  followed by hydrolysis yields (1)  $\alpha,\alpha$ -dichloroacetone (3:5430) + methylglyoxal (propanone-2-al-1) [Beil. I-762; I<sub>r</sub>-(395), I<sub>r</sub>-(819)].

3:7480 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **8**, 1232-1246 (1938); *Cent.* 1939, II 4223; *C.A.* **33**, 4190 (1939).

3:7485 1-CHLORO-2-METHYLBUTENE-2  $\text{C}_4\text{H}_7\text{Cl}$  Beil. I—  
( $\beta,\gamma$ -Dimethylallyl chloride)  $\text{CH}_3-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2\text{Cl}$  I<sub>r</sub>—  
I<sub>r</sub>-(189)

B.P. 110° at 760 mm. (1)

$D_4^{20} = 0.9327$  (1)

108-110° (2)

$n_D^{20} = 1.4481$  (1)

25.9-26.4° at 25 mm. (1)

$D_4^{15} = 0.9324$  (2)

Note.  $\bar{\text{C}}$  by virtue of facile allylic transposition is in equilibrium with its synionic isomer 3-chloro-2-methylbutene-1 (3:7300); reactns. of  $\bar{\text{C}}$  therefore may also yield derivatives related to its isomer.

[For prepn. of  $\bar{\text{C}}$  (or its mixt. with the synionic 3-chloro-2-methylbutene-1 (3:7300)) by actn. of  $\text{Cl}_2$  as specified (1) on "tertiary amylene" (a mixt. consisting mainly of 2-methylbutene-2 (1:8220) with some 2-methylbutene-1 (1:8210)) see (1).—The relative amt. of  $\bar{\text{C}}$  and its isomer is not constant but usually is about 40% of  $\bar{\text{C}}$  with 60% of 3-chloro-2-methylbutene-1 (3:7300), the ratio, however, being independent of the proportion of the two olefins in the starting material.]

[For formn. of  $\bar{\text{C}}$  from 2-methylbutene-2 (1:8220) with  $\text{Cl}_2$  see (2); from 2-methylbutene-1 (1:8210) see (3); for prepn. of  $\bar{\text{C}}$  (together with other prods.) from 1-chloro-2-methylbutanol-2 (3:8175) by distn. with anhyd. oxalic acid (4) or with  $\text{Ac}_2\text{O}$  + conc.  $\text{H}_2\text{SO}_4$  (5) see (4) (5); for prepn. of  $\bar{\text{C}}$  from 2-methylbuten-2-ol-1 with  $\text{PCl}_5$  + pyridine see (1).]

$\bar{\text{C}}$  on hydrolysis gives not only the alc. corresponding to  $\bar{\text{C}}$  but also that corresp. to the isomeric 3-chloro-2-methylbutene-1 (3:7300) together with a little ketone: thus  $\bar{\text{C}}$  on hydrolysis with 12 pts. aq. at 70° for 16 hrs. gives (6) 25% alc. A (2-methylbuten-1-ol-3) [*N*-( $\alpha$ -naphthyl)carbamate, m.p. 91.5-93° (6)] + 50% alc. B (2-methylbuten-2-ol-1) [*N*-( $\alpha$ -naphthyl)carbamate, m.p. 103-103.5° (6)] + 5% isopropyl methyl ketone (1:5410);

## 3:7470 1-CHLOROPENTENE-2

 $C_5H_9Cl$ 

Beil. I —

(γ-Ethylallyl chloride)  $CH_3.CH_2.CH=CH.CH_2Cl$ I<sub>1</sub>—I<sub>2</sub>-(184)

B.P. 109-110°

(1) (2)

 $D_4^{25} = 0.9095$  (3)  $n_D^{25} = 1.4347$  (3)

109.5°

(3)

106-108°

(4)

 $D_4^{21.5} = 0.008$  (4)  $n_D^{21.5} = 1.4352$  (4)

62-63.2° at 148 mm. (5)

Note.  $\bar{C}$  by virtue of facile allylic transposition is readily converted to an equilibrium mixt. with its synionic isomer 3-chloropentene-1 (3:7260) q.v.; reactns. of  $\bar{C}$  may therefore frequently yield also the corresponding derivatives of the isomer.

[For prepn. of  $\bar{C}$  (or its mixt. with 3-chloropentene-1 (3:7260)) from penten-2-ol-1 with dry HCl gas at 0° (5) (7), with  $PCl_3$  + pyridine (4) (7), or with  $SOCl_2$  in ether (6) see indic. refs.; for prepn. of  $\bar{C}$  from 3-chloropentene-1 (3:7260) by htg. at 225° (60-62%  $\bar{C}$ ) see (6) (3).] [ $\bar{C}$  is separable from the accompanying isomer by careful fractional distn. (7) (5).] [For formn. of  $\bar{C}$  (together with other products) from pentene-2 (1:8215) +  $Cl_2$  in  $CCl_4$  see (8).]

$\bar{C}$  on long shaking with aq.  $Na_2CO_3$  gives (7) in poor yield penten-2-ol-1 (p-nitrobenzoate, m.p. 53°) accompanied by much penten-1-ol-3. —  $\bar{C}$  on htg. with alc. KOH gives (3) (7) in poor yield the corresp. ethyl ether, viz., 1-ethoxypentene-2, b.p. 123°,  $D_4^{23} = 0.7930$ ,  $n_D^{23} = 1.4099$  (3), accompanied by the isomeric 3-ethoxypentene-1, b.p. 102°,  $D_4^{23} = 0.7768$ ,  $n_D^{23} = 1.3886$  (3).

[For study of reactns. of  $\bar{C}$  with KOAc in AcOH, with AgOAc, with *N*-methylaniline, with diethylamine, etc., see (7); for reactn. of  $\bar{C}$  with phenol in pres. of  $K_2CO_3$  + acetone see (5).]

① *N*-(Penten-2-yl-1)phthalimide [*N*-(γ-ethylallyl)phthalimide]: colorless rhombic cryst. from alc., m.p. 69-70° (7). [From  $\bar{C}$  on htg. with K phthalimide in a s.t. at 190-200° for 2½ hrs.; note that some of the corresp. deriv. from the isomer, viz., *N*-(α-ethylallyl)phthalimide, m.p. 78-79°, is formed in extent of about 10% (7).]

3:7470 (1) Mumm, Richter, *Ber.* 73, 858-860 (1940). (2) Mumm, Hornhardt, Diederichsen, *Ber.* 72, 197 (1939). (3) Prevost, *Compt. rend.* 187, 1053-1054 (1928). (4) Gredy, *Bull. soc. chim.* (5) 4, 419 (1937). (5) Lauer, Filbert, *J. Am. Chem. Soc.* 58, 1388 (1936). (6) Prevost, *Bull. soc. chim.* (4) 49, 264-267 (1931). (7) Meisenheimer, Link, *Ann.* 479, 254-277 (1930). (8) Stewart, Weidenbaum, *J. Am. Chem. Soc.* 53, 98-100 (1930).

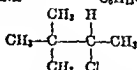
## 3:7475 3-CHLORO-2,2-DIMETHYLBUTANE

 $C_6H_{13}Cl$ 

Beil. S.N. 10

(Pinacolyl chloride;

ter-butyl-methyl-carbinyl chloride)



B.P. 109.0° at 734 mm. (1)

 $D_4^{20} = 0.8767$  (1)  $n_D^{20} = 1.4181$  (1)

[For formn. of  $\bar{C}$  (11%) from 2,2-dimethylbutane (neohexane) (1:8510) on chlorination see (1).] [Note that the corresp. alc. (pinacolyl alc.) (1:6186) with HCl does not give  $\bar{C}$  but rather rearr. prods. (2).]

$\bar{C}$  with Mg in dry ether gives  $RMgCl$  which with oxygen yields (1) pinacolyl alc. (1:6186) q.v.

① Pinacolyl mercuric chloride ( $C_6H_{13}HgCl$ ): cryst. from dil. alc., m.p. 89-90° (3); 89.5-90° (2). [From  $RMgCl$  +  $HgCl_2$  in ether.]

[For density of  $\bar{C}$  at 0°, 15°, 25°, 50°, and 65°, together with parachors at 0°, 25°, 50°, and 75°, see (9).]

[For prepn. of  $\bar{C}$  from corresp. alc., dimethyl-*n*-propyl-carbinol (2-methylpentanol-2) (1:6190) with  $PCl_5$  (6), with  $HCl$  gas (1) (2), or with conc.  $HCl$  (4) (5) see indic. refs.; for prepn. (68% yield) from ethyl-isopropyl-carbinol (2-methylpentanol-3) (1:6194) with  $HCl$  as the result of rearrangement see (1); for formn. (together with other products) from reaction of 2-ethylbutanol-1 (1:6223) with  $HCl + ZnCl_2$  see (3); for formn. from 2-methylpentene-2 (1:8275) by addn. of  $HCl$  see (7) (8).]

[For study of rate of reaction with  $KI$  in acetone see (5).]

$\bar{C}$  with  $Mg$  in dry ether yields  $RMgCl$ ; upon treatment with oxygen this gives (48% yield (1)) of dimethyl-*n*-propyl-carbinol (2-methylpentanol-2) (1:6190) q.v.

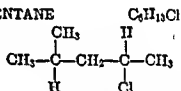
Ⓐ Dimethyl-*n*-propyl-acetanilide: m.p. 70.5–74° (3). [From  $\bar{C}$  via conversion to  $RMgCl$  and reaction with phenyl isocyanate (3).]

Ⓑ Dimethyl-*n*-propyl-acet- $\alpha$ -naphthalide: m.p. 116–118° (3). [From  $\bar{C}$  via conversion to  $RMgCl$  and reaction with  $\alpha$ -naphthyl isocyanate (3).]

3: 7490 (1) Whitmore, Johnston, *J. Am. Chem. Soc.* 60, 2267 (1938). (2) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938). (3) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938). (4) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938). (5) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938). (6) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938). (7) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938). (8) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938). (9) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938).

### 3: 7495 *d,l*-4-CHLORO-2-METHYLPENTANE

(*d,l*-Isobutyl-methyl-carbinyl  
chlorido)



Bell. I —

I<sub>1</sub> —

I<sub>2</sub>-(111)

B.P. 111–112° at 773 mm. (1)

$D_4^{20} = 0.801$  (1)  $n_D^{20} = 1.4113$  (1)

[For prepn. of  $\bar{C}$  from 2-methylpentanol-4 (1:6199) with dry  $HCl$  for 18 weeks (82% yield) see (1); for formn. of  $\bar{C}$  (together with other products) in reaction of 2-ethylbutanol-1 (1:6223) with  $HCl + ZnCl_2$  see (2).]

$\bar{C}$  with  $Mg$  in dry ether yields  $RMgCl$  which with  $O_2$  gives (62% yield (1)) 2-methylpentanol-4 (1:6199) [*N*-( $\alpha$ -naphthyl)carbamate, m.p. 03.5–04.5° (2)]; this alc. upon oxidn. with  $CrO_3/H_2SO_4$  yields (2) 4-methylpentanone-2 (1:5430) q.v.

3: 7495 (1) Whitmore, Johnston, *J. Am. Chem. Soc.* 60, 2267 (1938). (2) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938).

$\bar{C}$  on hydrolysis with 2 pts. aq. + 1 mole  $\text{CaCO}_3$  for 4 hrs. at  $70^\circ$  gives (6) 60% alc.  $A$  + 30% alc.  $B$  + 5% isopropyl methyl ketone (1:5410);  $\bar{C}$  on hydrolysis with  $\text{CaO}$  for  $1\frac{1}{2}$  hrs. gives (6) 70% alc.  $A$  + 25% alc.  $B$  + a trace of ketone.

[For study of reactn. of  $\bar{C}$  with  $\text{NaI}$  (4) and its rate of reactn. with  $\text{KI}$  in acetone at  $20^\circ$  (7) or with  $\text{NaOEt}$  in alc. at  $35^\circ$  (7) see indic. refs.; the reactivity of the halogenation of  $\bar{C}$  is greater than that in crotyl chloride (1-chlorobutene-2) (3:7205) and the latter in turn is more reactive than that in methallyl chloride (3-chloro-2-methylpropene-1) (3:7145) or allyl chloride (3:7035), which are about the same (4).]

$\bar{C}$  on treatment with  $\text{O}_3$  followed by hydrolysis yields (3) (2) chloroacetone (3:7212) + acetaldehyde (1.0100).

3:7485 (1) Buign, Engs, Groll, Hearne, *Ind Eng. Chem.* **31**, 1416 (1939). (2) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **6**, 1116-1133 (1936); *Cent.* **1937**, **1** 572. *C.A.* **31**, 1003 (1937). (3)

### 3:7487 ALLYL CHLOROFORMATE



Beil. III - 12

(Allyl chlorocarbonate)  $\text{Cl.CO.O.CH}_2\text{CH=CH}_2$

III<sub>1</sub>—

III<sub>2</sub>-(11)

B.P.  $110-111.5^\circ$  at 765 mm. (1)

$110^\circ$  (2)

Note that the prod. of b.p.  $180^\circ$ , formerly (3) supposed to have been  $\bar{C}$ , is in fact (2) diallyl carbonate.

[For prepn. of  $\bar{C}$  from allyl alc. (1:6145) with phosgene (3:5000) (yield 37% (1)) (4) (2) see indic. refs.; note that some diallyl carbonate, b.p.  $166^\circ$  at 730 mm. (2), is also formed (2).]

$\bar{C}$  in quinoline begins to decompose at  $37^\circ$  (5) (6) presumably into  $\text{CO}_2$  + allyl chloride (3:7035) although this is not specifically stated.

[For reaction of  $\bar{C}$  with diethylene glycol (1:6525), triethylene glycol (1:6538), etc., see (7).]

3:7487 (1) Schving, Sabetay, *Bull. soc. chim.* (4) **43**, 858 (1925). (2) Fierz-David, Müller, *J. Chem. Soc.* **125**, 26 (1924) (3) Thiele, *Dent. Ann.* **302**, 262 (1898). (4) Schving, French **34**, 412, June 18, 1929, *Cent.* **1929**, II 2829. (5) Carré, *Bull. soc. chim.* (5) **3**, 1072 (1936) (6) Carré, Passedouet, *Compt. rend.* **201**, 899 (1935). (7) Muskat, Strain (to Pittsburgh Plate Glass Co.), U.S. 2,370,565, Feb. 27, 1945; *C.A.* **39**, 4526 (1945).

### 3:7490 2-CHLORO-2-METHYLPENTANE

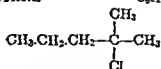
(Dimethyl-*n*-propyl-carbonyl chloride)



Beil. I - 148

I<sub>1</sub>-(53)

I<sub>4</sub>-(111)



B.P.

$110-111^\circ$  dec. at 734 mm. (1)

$D_4^{20} = 0.863$  (1)

$110-113^\circ$  (2)

$64.5-64.7^\circ$  at 160 mm. (3)

$D_4^{15} = 0.8678$  (2)

$50-53^\circ$  at 41 mm. (4)

$n_D^{20} = 1.4126$  (3); cf. (1)

$36-37^\circ$  at 15 mm. (5)

$n_D^{16.5} = 1.4176$  (2)

$\bar{C}$  decomposes considerably if distd. at ord. press. (3).

[For prepn. (93% yield (2)) from paraldehyde (1:0170) + *n*-propyl alc. (1:6150) + dry HCl see (2) (3).]

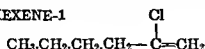
$\bar{C}$  on stdg. polymerizes to dark tarry residue (2).

[ $\bar{C}$  on bromination yields  $\alpha,\beta$ -dibromoethyl *n*-propyl ether (3).]

$\bar{C}$  on shaking with aq. yields acetaldehyde (1:0100), *n*-propyl alc. (1:6150) + HCl.

3:7525 (1) Gauthier, *Ann. chim.* (8) **16**, 312 (1909). (2) Henze, Murchison, *J. Am. Chem. Soc.* **53**, 4077-4079 (1931). (3) Dykstra, Lewis, Boord, *J. Am. Chem. Soc.* **52**, 3399-3400 (1930).

## 3:7530 2-CHLOROHEXENE-1

 $\text{C}_6\text{H}_{11}\text{Cl}$ 

Beil. S.N. 11

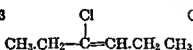
B.P.  $113^\circ$  at 740 mm. (1)  $D_4^{25} = 0.8886$  (1)  $n_D^{25} = 1.4278$  (1)  
 $109.5-110.5^\circ$  at 735 mm. (2)  $0.8872$  (2)  $1.4187$  (2)

[For prepn. of  $\bar{C}$  from hexyne-1 (1:8055) with dry HCl +  $\text{BiCl}_3$  in  $\text{C}_6\text{H}_6$  (20% yield (1) together with 40% yield 2,2-dichlorohexane (3:9342)) or with  $\text{AcCl}$  +  $\text{SnCl}_4$  (15% yield (2) together with 37% 4-chloro-octen-3-one-2, b.p.  $75-95^\circ$  at 20 mm.) see (1) (2); for prepn. of  $\bar{C}$  (60.5% yield (1)) from 2,2-dichlorohexane (3:9342) with KOH in *n*-propyl alc. at  $95^\circ$  see (1).]

$\bar{C}$  in  $\text{CCl}_4$  +  $\text{SbCl}_5$  treated with  $\text{Cl}_2$  at  $35-40^\circ$  gives (1) (3) *cis*-1,2-dichlorohexene-1 (3:9330) (26.7% yield (1)) together with 25.4% 1,1,2,2-tetrachlorohexane (3:9332).

3:7530 (1) Hennion, Walsh, *J. Am. Chem. Soc.* **62**, 1367-1368 (1940). (2) Kroeger, Sowa, Nieuwland, *J. Org. Chem.* **1**, 163-169 (1936). (3) Norris, Hennion, *J. Am. Chem. Soc.* **62**, 450 (1940).

## 3:7535 3-CHLOROHEXENE-3

 $\text{C}_6\text{H}_{11}\text{Cl}$ 

Beil. S.N. 11

B.P.  $113.0-113.5^\circ$  at 748 mm. (1)  $D_4^{25} = 0.8898$  (1)  $n_D^{25} = 1.4320$  (1)

Two geom. stereoisomers of  $\bar{C}$  are possible, but only this one is as yet recognized.

[For prepn. of  $\bar{C}$  from hexyne-3 (diethylacetylene) (1:8065) with  $\text{AcCl}$  +  $\text{SnCl}_4$  see (1); (both *cis* and *trans* stereoisomers of 4-chloro-3-ethylhexen-3-one-2 are also formed).]

3:7535 (1) Kroeger, Sowa, Nieuwland, *J. Org. Chem.* **1**, 163-169 (1936).

3:7540 *n*-PROPYL CHLOROFORMATE $\text{C}_4\text{H}_7\text{O}_2\text{Cl}$ 

Beil. III - 11

(n-Propyl chlorocarbonate)

 $n\text{-C}_3\text{H}_7\text{O.CO.Cl}$ 

III-(6)

III-(10)

B.P.  $114-115.5^\circ$  at 768 mm. (1)  $D_4^{20} = 1.0901$  (1)  $n_D^{20} = 1.40350$  (4)  
 $115.2$  cor. (2) (3)

$\bar{C}$  reacts but slowly with cold aq., more rapidly on warming, yielding *n*-propyl alc. (1:6150) +  $\text{CO}_2$  + HCl.

[For prepn. from *n*-propyl alc. (1:6150) + phosgene (3:5000) (42% yield (3)) see (2) (3).]

$\bar{C}$  on htg. with  $\text{ZnCl}_2$  yields (5) propylene,  $\text{CO}_2$  + HCl;  $\bar{C}$  on warming with pyridine or quinoline dec. at  $66^\circ$  into *n*-propyl chloride (3:7040) +  $\text{CO}_2$  (6) cf. (7).

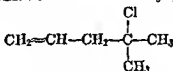
## CHAPTER XVII

### DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

#### Section 2. $D_4^{20}$ less than 1.1500

(3:7500-3:7999)

3:7500 4-CHLORO-4-METHYLPENTENE-1  $C_6H_{11}Cl$  Beil. I - 217  
 (2-Chloro-2-methylpentene-4)  
 (Allyl-dimethyl-carbinyl  
 chloride)



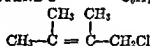
$I_1-$   
 $I_2-$

B.P. 109-114° s.l. dec. (1)

[For prepn. of  $\bar{C}$  from 2-methylpenten-4-ol-2 (allyl-dimethyl-carbinol) [Beil. I-445,  $I_2$  (487)] with  $PCl_5$  see (1).]

3:7500 (1) M. Saytzeff, A. Saytzeff, *Ann.* 185, 156 (1877).

3:7520 1-CHLORO-2,3-DIMETHYLBUTENE-2  $C_6H_{11}Cl$  Beil. S.N. 11  
 ( $\beta,\gamma,\gamma$ -Trimethylallyl chloride)



B.P. 111-112° at 756 mm. (1)

$D_4^{19} = 0.8895$  (1)  $n_D^{19} = 1.4315$  (1)

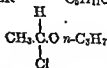
Note.  $\bar{C}$  by virtue of allylic transposition would be expected to be in equilibrium with its synionic isomer 3-chloro-2,3-dimethylbutene-1 ( $\alpha,\alpha,\beta$ -trimethylallyl chloride). The material described by (1) was regarded as  $\bar{C}$ ; the isomer seems to be unrecorded.

[For prepn. of  $\bar{C}$  (or its mixt. with 3-chloro-2,3-dimethylbutene-1) in 90% yield from 2,3-dimethylbutene-2 (tetramethylethylene) (1:8290) with  $Cl_2 + NaHCO_3$  at 0° see (1).]

$\bar{C}$  on hydrolysis yields (1) a hexenol (regarded (1) as 2,3-dimethylbuten-1-ol-3 derived from the synionic isomer of  $\bar{C}$ ), b.p. 116-118°,  $D_4^{17} = 0.835$ ,  $n_D^{17} = 1.4248$  (1).

3:7520 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, II 4222; *C.A.* 33, 4190 (1939).

3:7525  $\alpha$ -CHLOROETHYL *n*-PROPYL ETHER  $C_6H_{11}OCl$  Beil. I - 607



$I_1-$   
 $I_2-$

B.P. 112-115° at 731 mm. (1)  
 47.5° cor. at 40 mm. (2)

$D_4^{20} = 0.9322$  (2)  $n_D^{20} = 1.4013$  (2)



[ $\bar{C}$  on passing over alkali (NaOH,  $K_2CO_3$ , soda-lime, etc.) at elevated temperatures (e.g., 700-750°) yields (6) butadiene-1,3.]

[ $\bar{C}$  with boilg. satd. *n*-BuOH/KOH loses 1 HCl giving (64% yield (9)) 1-chlorobutene-1 (3:7110).]

3:7550 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, II 4223. (2) Kohlrusch, Köppl, *Monatsh.* 65, 197 (1935). (3) Meyer, Petrenko-Kritschenko, *Ber.* 25, 3308 (1892). (4) Henne, Renoll, Leicester, *J. Am. Chem. Soc.* 61, 940 (1939). (5) Muskat (to du Pont), U.S. 2,038,593, April 28, 1936; *Cent.* 1936, II 3358. (6) Muskat (to du Pont), U.S. 2,070,609, Feb. 16, 1937; *Cent.* 1937, II 2597. (7) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 7, 893-896 (1937); *C.A.* 31, 5755 (1937); *Cent.* 1938, II 2575. (8) Muskat, Northrup, *J. Am. Chem. Soc.* 52, 4050-4052 (1930). (9) Henne, Hinkamp, *J. Am. Chem. Soc.* 67, 1197 (1945).

3:7555 4-CHLORO-2,2-DIMETHYLBUTANE  $\begin{array}{c} \text{CH}_3 \quad \text{C}_6\text{H}_{13}\text{Cl} \\ | \quad \vdots \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_2-\text{Cl} \\ | \\ \text{CH}_3 \end{array}$  Beil. S.N. 10  
(Neopentylcarbinyl chloride)

B.P. 115° (1) (2)

41° at 50 mm. (2) (3)

$D_4^{20} = 0.8670$  (2)  $n_D^{20} = 1.4161$  (1)

1.4160 (2) (3)

[For prepn. of  $\bar{C}$  (60% yield) from corresp. alc. (neopentylcarbinol) (1:6219) with  $\text{SOCl}_2$  + pyridine see (1); for prepn. of  $\bar{C}$  from *ter*-butyl chloride (3:7045) + ethylene in presence of  $\text{AlCl}_3$  (75% yield),  $\text{FeCl}_3$  (57% yield), or  $\text{BiCl}_3$  (6-30% yield) see (2).]

$\bar{C}$  with Mg + dry ether yields  $\text{RMgCl}$  which with oxygen yields (1) (2) neopentylcarbinol (1:6219) q.v.

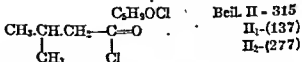
① Neopentylcarbinyl mercuric chloride ( $\text{C}_5\text{H}_{13}\text{HgCl}$ ): m.p. 133-133.5° (1). [From  $\text{RMgCl} + \text{HgCl}_2$  (1).]

②  $\gamma,\gamma$ -Dimethyl-*n*-valeranolide: ndls. from dil. alc., m.p. 138-139° (2). [From  $\bar{C}$  via conversion to  $\text{RMgCl}$  and reaction with phenyl isocyanate (2).]

3:7555 (1) Whitmore, Bernstein, *J. Am. Chem. Soc.* 60, 2626-2628 (1938). (2) Schmerling, *J. Am. Chem. Soc.* 67, 1152-1154 (1945). (3) Schmerling, *J. Am. Chem. Soc.* 67, 1782-1783 (1945).

3:7560 ISOVALERYL CHLORIDE

( $\beta$ -Methyl-*n*-butyryl chloride)



Beil. II - 315

$\Pi_1$ -(137)

$\Pi_2$ -(277)

B.P.

[117.9° at 766 mm. (1)]

114.5-115.5° at 771 mm. (2)

115.5° at 741 mm. (3)

114.3-115.7° (4)

114.5-115.5° (5)

113.5-114.5° at 725.7 mm. (5)

$D_4^{25} = 0.9854$  (2)  $n_D^{25} = 1.41361$  (2)

$D_4^{20} = 0.9887$  (6)  $n_D^{20} = 1.4157$  (3)

0.9862 (3) 1.41555 (6)

0.9844 (1) 1.41488 (1)

[For prepn. of  $\bar{C}$  from isovaleric acid (1:1050) with  $\text{PCl}_3$  (7) (8) (9), with  $\text{PCl}_3 + \text{ZnCl}_2$  (79% yield (10)), with  $\text{SOCl}_2$  (72% yield (10)) (1) (5) see indic. refs.; note that use of  $\text{PCl}_5$  is inadvisable since the by-prod.,  $\text{POCl}_3$ , boils too close to  $\bar{C}$ .]

[ $\bar{C}$  htd. with K isovalerate yields (11) isovaleric anhydride [Beil. II-314,  $\Pi_1$ -(137),  $\Pi_2$ -(277)], b.p. 215.1-215.3° at 762 mm., 102-103° at 15 mm. (11),  $D_4^{20} = 0.9327$ ,  $n_D^{20} = 1.4043$  (12).]

③ *n*-Propyl *N*-phenylcarbamate (*n*-propyl carbanilate) [Beil. XII-321]: from  $\bar{C}$  + excess aniline in ether, cryst. from alc., m.p. 57-59° (8).

3:7540 (1) Karvonen, *Ann. Acad. Sci. Fennicae A-10*, No. 4, 19 (1916); *Cent.* 1919, III 808. (2) Roese, *Ann.* 205, 227-230 (1850). (3) Hamilton, Sly, *J. Am. Chem. Soc.* 47, 436-437 (1925). (4) Dobrosserdow, *Cent.* 1911, I 954. (5) Underwood, Bard, *J. Am. Chem. Soc.* 53, 2201 (1931). (6) Carré, *Bull. soc. chim.* (5) 3, 1069 (1936). (7) Fry, *J. Am. Chem. Soc.* 36, 260-261 (1914). (8) Roemer, *Ber.* 6, 1103 (1878).

3:7545 CHLOROCYCLOPENTANE  $\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ | \quad \diagup \\ \text{H}_2\text{C}-\text{CH}_2 \end{array} \text{C} \begin{array}{l} \text{H} \\ \diagdown \\ \text{Cl} \end{array}$   $\text{C}_5\text{H}_9\text{Cl}$  Beil. V - 10  
(Cyclopentyl chloride)  $V_1-$  (4)  
 $V_2-$  (4)

B.P. 114-115.5° cor. (1)  $D_4^{20} = 1.0051$  (1) (2)  $n_D^{20} = 1.4510$  (1)  
114-115° at 748 mm. (2) 1.005 (4) 1.4509 (2)  
114.1-114.9° (3)  
114° (4)

[For prepn. of  $\bar{C}$  from cyclopentanol (1:6412) with boilg. conc. HCl +  $\text{CaCl}_2$  (87% yield (5)) (6), or with conc. HCl at 110° (87% yield (2)) (1) (7) (8), or with  $\text{PCl}_3$  at 0° (3) (4) see indic. refs.] [Some cyclopentene (1:8037), b.p. 34°, may also be formed but is readily sepd. by distn.] [For prepn. of  $\bar{C}$  from cyclopentane (1:8400) with  $\text{Cl}_2$  see (13).]

$\bar{C}$  over  $\text{BaCl}_2$  at 300-400° at 15-20 mm. yields (9) cyclopentene (1:8037).

[ $\bar{C}$  with  $\text{C}_6\text{H}_6$  +  $\text{AlCl}_3$  gives (54% yield (10)) phenylcyclopentane (cyclopentylbenzene), b.p. 217°,  $D_4^{20} = 0.9474$ ,  $n_D^{20} = 1.5280$  (10); for reactn. of  $\bar{C}$  with 2-methylpyridine ( $\alpha$ -picoline) see (11); for reactn. of  $\bar{C}$  with  $\text{Na}_2\text{SO}_3$  at 200° see (4).]

$\bar{C}$  with Mg in dry ether gives (1) (2) (5) (7) cyclopentyl  $\text{MgCl}$ ; this with  $\text{CO}_2$  gives (1) (7) cyclopentanecarboxylic acid [Beil. IX-6], b.p. 215.5-216° cor.,  $D_4^{20} = 1.0510$ ,  $n_D^{18} = 1.4534$  (1) (amide, lfts. from MeOH, m.p. 179° cor. (1), 178° (12)).]

④ Cyclopentyl mercuric chloride  $\text{C}_5\text{H}_9\text{HgCl}$ : m.p. 108.5° (4). [The method of formn. of this deriv. is not stated but is presumably from  $\text{RMgCl} + \text{HgCl}_2$ .]

3:7545 (1) Zelinskii, *Ber.* 41, 2627-2628 (1908). (2) Zelinskii, Mikhlin, Eventova, *Ber.* 66, 1422-1426 (1933). (3) Kohlrausch, Reitz, Stockmair, *Z. physik. Chem. B-32*, 235 (1936). (4) Turkiewicz, Pilat, *Ber.* 71, 284-285 (1938). (5) Pilat, Turkiewicz, *Ber.* 72, 1527-1531 (1939). (6) Yarnall, Wallis, *J. Org. Chem.* 4, 287 (1939). (7) Neunhoffer, Schluter, *Ann.* 526, 70 (1936). (8) Canals, Mousseron, Granger, Gastaud, *Bull. soc. chim.* (5) 4, 2048 (1937). (9) Badische Anilin u. Sodafabrik, *Ger.* 255,638, Jan. 3, 1913, *Cent.* 1913, I 477. (10) Zelinskii, Titz, *Ber.* 64, 185 (1931).

(11) Tschutschibabine, *Bull. soc. chim.* (5) 5, 435 (1938). (12) Nenitzescu, Cantunari, *Ber.* 65, 811 (1932). (13) Bailey, McAllister (to Shell Development Co.), U.S. 2,342,072, Feb. 15, 1944; *C. A.* 38, 4621 (1944).

3:7550 1,1-DICHLOROBUTANE  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCl}_2$   $\text{C}_4\text{H}_8\text{Cl}_2$  Beil. I - 119  
(*n*-Butylidene (di)chloride)  $I_1-$   
 $I_2-$

B.P. 114.5-115° at 763 mm. (1)  $D_4^{20} = 1.0863$  (7)  $n_D^{20} = 1.4355$  (7)  
113.8-113.9° (2)  
113-115° (3) (7)

[For prepn. (47% yield (4)) from *n*-butyraldehyde (1:0130) by actn. of  $\text{PCl}_5$  (39% yield (9)) see (1) (2) (3) (9); for formn. from butane by chlorination see (5) (6); for formn. from *n*-butyl chloride (3:7160) on chlorination see (7) (8).]

[ $\bar{C}$  with equal wt. ethyl mercaptan gives (34% yield (33)) 1,3-bis-(ethylmercapto)-propanone-2, b.p. 117–121° at 15 mm. (33) (corresp. semicarbazone, m.p. 98–99°), but  $\bar{C}$  with large excess ethyl mercaptan (4 wt. pts.) gives also 1,2,2,3-tetra(ethylmercapto)-propane, oil (33). —  $\bar{C}$  (1 mole) with benzyl mercaptan (2 moles) in alc. NaOH yields (34) 1,3-bis-(benzylmercapto)propanone-2, nil, which on oxidn. in acid soln. with  $KMnO_4$  gives the corresp. disulfone, ndls. from alc., m.p. 182° (34).] — [For reactn. of  $\bar{C}$  with alk. sulfides and/or polysulfides in prepa. of resins see (37).]

$\bar{C}$  with KI even at room temp. (7) yields 1,3-diiodoacetone, pr. from acetone, m.p. 61°. [For reaction of  $\bar{C}$  with  $MeMgBr$  as means of prepa. of *sym.*-dichloro-*ter*-butyl alcohol (3:5977) see the latter.]

[ $\bar{C}$  with excess conc. aq. or liq. HCN in alc. at 30° for 12 hrs. (11) cf. (35) or with 25% HCN in pres. of a little  $NH_4OH$  (36) yields  $\beta,\beta'$ -dichloro- $\alpha$ -hydroxyisobutyronitrile (not isolated), which on hydrolysis with HCl (11) (35) (36) gives the corresp. acid,  $\beta,\beta'$ -dichloro- $\alpha$ -hydroxyisobutyric acid, m.p. 91–92° (11).]

[ $\bar{C}$  with diazotized aniline in pres. of  $NaOAc$  yields (3) 1,3-dichloro-1-(benzenecazo)-propanone-2, red-or. cryst. from hot alc., m.p. 156–157° (3); for corresp. homologs using diazotized *o*-toluidine or *p*-toluidine see (3).]

[ $\bar{C}$  with equiv. molar quant. thioacetamide in acetone or alc. followed by htg. with  $ZnCl_2$  (38) (39) gives 4-(chloromethyl)-2-methylthiazole hydrochloride (free base is oil, b.p. 65–67° at 3 mm. (38) (39)); for polymerization of this prod. by htg. see (38). —  $\bar{C}$  with thiobenzamide in acetone followed by htg. of resultant intermediate with HCl in acetone gives 4-(chloromethyl)-2-phenylthiazole hydrochloride (yields: 80–81% (40) (41)) (corresp. free base, m.p. 51° (40), 48.2–51.2° cor. (41)); for reactns. of this prod. see (41). — For analogous reactn. of  $\bar{C}$  with many other substituted thiobenzamides to give corresp. substituted thiazoles see (40) (39).]

[ $\bar{C}$  with equiv. molar amt. carbamyl chloride in dry ether at room temp. for 15 min. is claimed (2) to yield  $\beta,\beta'$ -dichloroisopropyl carbamate ("Aleudrin"), white cryst. from alc., m.p. 80–81° (2);  $\bar{C}$  with 2 molar equivs. of carbamyl chloride similarly treated is claimed (2) to yield  $\beta,\beta'$ -dichloroisopropyl allophanate, cryst. from 60% alc., m.p. 182° (2); note, however, that in view of the facts that the  $\bar{C}$  used in the cited work was obt'd. from 1,3-dichloropropanol-2, that the b.p.'s of this precursor and  $\bar{C}$  are almost identical, and that the  $\bar{C}$  employed was purified only by distillation, the indicated esters may have been due to the presence of unoxidized starting material.]

① 1,3-Dichloropropanone-2 semicarbazone: m.p. 120° (23). [Note that this prod. is very sensitive to heat (care in recrystn. from aq. or  $C_6H_6$ ) and is also changed by stdg. in solution (23).]

② 1,3-Dichloropropanone-2 4-(*p*-bromophenyl)semicarbazone: ndls. from alc., m.p. 196° cor. dec. (42). [From  $\bar{C}$  + 4-(*p*-bromophenyl)semicarbazide in alc. refluxed for 12 hrs. (42).]

③ Condensation product ( $C_{17}H_{19}O_4N_3SCH_3$ ) of  $\bar{C}$  with *N*-methyl-3-(carbohydrazido)-pyridinium *p*-toluenesulfonate: cryst. from 1:1 alc./ether, m.p. 115° cor. (43). [From  $\bar{C}$  with nicotinic acid hydrazide metho-*p*-toluenesulfonate in abs. alc. on refluxing for 15 mins. (43).]

3:0563 (1) Markownikow, *Ann.* 208, 353–358 (1881). (2) Sen, Barat, *J. Indian Chem. Soc.* 2, 77–81 (1925). (3) Favrel, *Bull. soc. chim.* (5) 1, 983–986, 989 (1934). (4) Posner, Rohde, *Ber.* 42, 3237–3242 (1909). (5) Edwards, Evans, Watson, *J. Chem. Soc.* 1937, 1944. (6) Glutz, Fischer, *J. prakt. Chem.* (2) 4, 54–55 (1871). (7) von Hoerman, *Ber.* 13, 1706–1709 (1880). (8) Cloez, *Ann. chim.* (6) 9, 167–170 (1886). (9) Erlenbach, *Ann.* 269, 46–48 (1892). (10) Conant, Quayle, *Org. Syntheses*, Coll. Vol. 1 (2nd ed.), 211–213 (1941); Coll. Vol. 1 (1st ed.), 206–207 (1932); 2, 13–15 (1922).

$\bar{C}$  with  $Cl_2$  in  $CCl_4$  yields (8)  $\alpha$ -chloroisovaleryl chloride (3:8144), b.p. 148-149° (together with some  $\beta$ -chloroisovaleryl chloride).]

$\bar{C}$  on cat. hydrogenation using Pd as specified (13) gives 95% yield isovaleraldehyde (1:0140), b.p. 92° (13) (use of  $PtO_2$  gives (14) only small yield).]

[For reactn. of  $\bar{C}$  with acetylene +  $AlCl_3$  in pet. eth. at 0-5°, yielding on treatment with aq.  $\beta$ -chlorovinyl isobutyl ketone, b.p. 63-65°, see (15); with cyclohexene +  $AlCl_3$  in cyclohexane yielding cyclohexyl isobutyl ketone, b.p. 216-219°,  $D_4^{20} = 0.8867$ ,  $n_D^{20} = 1.58155$ , see (16); with sodium azide in benzene yielding isobutyl isocyanate see (17).]

$\bar{C}$  on hydrolysis yields isovaleric acid (1:1050), b.p. 176.5°. — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see isovaleric acid (1:1050).

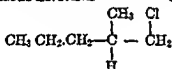
3:7560 (1) Leimu, *Ber.* 70, 1049 (1937). (2) von Auwers, Schmidt, *Ber.* 46, 474 (1913). (3) Martin, Partington, *J. Chem. Soc.* 1936, 162. (4) Kohlrausch, Pongratz, *Z. physik. Chem.* B-22, 382 (1933). (5) Bardan, *Cent.* 1932, II 354. (6) Brühl, *Ann.* 203, 24 (1880). (7) Béchamp, *Jahresber.* 1856, 429. (8) Michael, *Ber.* 34, 4055-4056 (1901). (9) Scheuble, *Ger.* 251,806, Oct. 8, 1912; *Cent.* 1912, II 1503. (10) Clark, Bell, *Trans. Roy. Soc. Can.* (3) 27, III, 97-103 (1933).

(11) Verkade, *Rec. trav. chim.* 36, 197 (1916). (12) Tromp, *Rec. trav. chim.* 41, 299 (1921). (13) Froschl, Danoff, *J. prakt. Chem.* (2) 144, 221-222 (1935). (14) Grignard, Mingasson, *Compt. rend.* 185, 1176 (1927). (15) Nelles, Baeyer (to I.G.), Brit 461,080, March 11, 1937; *Ger.* 642,147, Feb. 25, 1937, *Cent.* 1937, II 2597, *C.A.* 31, 4676 (1937). (16) Nenitzescu, Cioranescu, *Ber.* 69, 1823 (1936). (17) Naegeli, Gröntuch, Lendorff, *Helv. Chim. Acta* 12, 247-248 (1929).

### 3:7563 *d,l*-1-CHLORO-2-METHYLPENTANE

 $C_5H_{11}Cl$ 

Beil. I —


 $I_1 -$ 
 $I_2 - (111)$ 

B.P. 110-120° (1)

[For prepn. of  $\bar{C}$  from levorotatory 2-methylpentanol-1 with  $PCl_5$  in  $CHCl_3$  or from dextrorotatory 2-methylamylamine with  $NOCl$  see (1).]

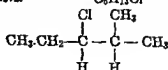
3:7563 (1) Levene, Mikesa, *J. Biol. Chem.* 84, 579-580 (1929).

### 3:7565 *d,l*-3-CHLORO-2-METHYLPENTANE

(Ethyl-isopropyl-carbinyl chloride)

 $C_5H_{11}Cl$ 

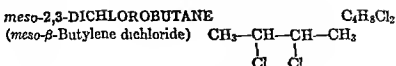
Beil. I - 148


 $I_1 -$ 
 $I_2 - (111)$ 

B.P. 115-116.5° dec. at 752 mm. (1)

[For prepn. of  $\bar{C}$  from 2-methylpentanol-3 (1:6194) with  $PCl_5$  see (1).]

3:7565 (1) Grigorowitsch, Pavlov, *J. Russ. Phys.-Chem. Soc.* 23, 166 (1891).

3:7580 *meso*-2,3-DICHLOROBUTANE*(meso*- $\beta$ -Butylene dichloride)

Beil. I —

I<sub>1</sub>—I<sub>2</sub>-(82)

B.P.

F.P.

116.0°	(1) (2)	-80.4° (1)	$D_4^{25} = 1.1023$ (6)	
115.9°	at 760 mm. (3)		$n_D^{25} = 1.4395$ (6)	
115.5-116.5° cor.	at 746 mm. (4)			1.4392 (6)
114-116°	(5)			1.4386 (6)
113.14°	at 746 mm. (6)			1.4385 (6)
49.52°	at 80 mm. (6)		$D_4^{20} = 1.1134$ (5)	
49.0-50.5°	at 80 mm. (7)		1.1067 (2)	
49.4-49.7°	at 80 mm. (6)		$n_D^{20} = 1.4413$ (2)	
48.5-49.0°	at 80 mm. (6)			1.443 (5)

[See also *d,l*-2,3-dichlorobutane (3:7615).]

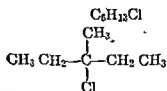
[For prepn. of  $\bar{C}$  from *trans*-butene-2 with  $\text{Cl}_2$  in light (63% yield (6)) (7) cf. (5) indic. refs.; for formn. of  $\bar{C}$  from *d,l*-erythro-3-chlorobutanol-2 (3:8004) (16% yield (6)) or from (+) *threo*-3-chlorobutanol-2 (3:8002) (15% yield (6)) with  $\text{SOCl}_2$  see (6) (note that from *d,l*-erythro-3-chlorobutanol-2 with  $\text{PCl}_5$  in  $\text{CHCl}_3$  a mixt. of  $\bar{C}$  + its *d,l*-isomer (3:7615) is obtd. (6)); for formn. of  $\bar{C}$  from *d,l*-2-chlorobutane (3:7125) with  $\text{Cl}_2$  in light (42.7% yield) see (2).]

[ $\bar{C}$  with  $\text{Cl}_2$  (slight excess) in dark at  $-17^\circ$  gives (5) 36.5% 1,2,3-trichlorobutane (3:5935) + 18% 2,2,3-trichlorobutane (3:5680).]

[ $\bar{C}$  with alc. KOH gives same results as does the *d,l*-isomer (3:7615) (3).]

3:7580 (1) Timmermans, *Bull. soc. chim. Belg.* 36, 504 (1927). (2) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 7, 663-666 (1937); *Cent.* 1937, II 372; *C.A.* 31, 5784 (1937). (3) Nave, *Bull. soc. chim. Belg.* 39, 435-439 (1930). (4) Lucas, Simpson, Carter, *J. Am. Chem. Soc.* 47, 1467 (1925). (5) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 6, 1553-1558 (1936); *Cent.* 1937, I 3785; *C.A.* 31, 2165 (1937). (6) Lucas, Gould, *J. Am. Chem. Soc.* 63, 2541-2545 (1941). (7) Taufen, Murray, Cleveland, *J. Am. Chem. Soc.* 65, 1131-1132 (1943).

## 3:7585 3-CHLORO-3-METHYLPENTANE

*(Diethyl-methyl-carbinyl chloride)*

Beil. I - 149

I<sub>1</sub>-(54)I<sub>2</sub>-(112)

B.P.

B.P. (contd.)

116°	(1)	85° at 280 mm. (5)	$D_4^{20} = 0.8900$ (4)	
115-118°	(2)	69.5° at 160 mm. (6)	$n_D^{20} = 1.4210$ (3)	
115-117°	(3)	68-69° at 160 mm. (7)		1.4208 (7)
117-118° at 760 mm. (4)		35° at 25 mm. (4)		1.4202 (6)
111° at 761 mm. (5)			$D_4^{14} = 0.8893$ (1)	
			0.878 (3)	
			$n_D^{17} = 1.4215$ (3)	

[For density of  $\bar{C}$  at  $0^\circ$ ,  $15^\circ$ ,  $25^\circ$ ,  $50^\circ$ , and  $65^\circ$  together with parachors at  $0^\circ$ ,  $25^\circ$ , and  $50^\circ$  see (9).]

[For prepn. of  $\bar{C}$  from corresp. alc., diethyl-methyl-carbinol (3-methylpentanol-3) (1:6189), with  $\text{PCl}_5$  (8),  $\text{HCl}$  gas (1) (2) at  $0^\circ$  (5) or  $10$ - $15^\circ$  (59% yield (7)) see indic. refs.]

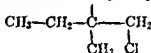
with diphosgene (3:5515) see (4); for formn. from 3-methylpentene-2 (1:8260) + conc. HCl see (3); for formn. (together with other products) during reaction of 2-ethylbutanol-1 (1:6223) with HCl +  $\text{ZnCl}_2$  see (6).]

$\bar{\text{C}}$  with Mg in dry ether yields (7) corresp.  $\text{RMgCl}$ .

① Diethyl-methyl-acetanilide: m.p. 86.5-89.5° (6). [From  $\bar{\text{C}}$  via conversion to  $\text{RMgCl}$  and reaction with phenyl isocyanate (6).]

3:7585 (1) Schreiner, *J. prakt. Chem.* (2) 82, 295 (1910). (2) Gilman, Schulze, *J. Am. Chem. Soc.* 49, 2330 (1927). (3) Nasarow, *Ber.* 70, 621 (1937). (4) Nekrassow, Melnikow, *J. prakt. Chem.* (2) 127, 217-218 (1930). (5) Favorskii, Zalesku-Kibardine, *Bull. soc. chim.* (4) 37, 1230 (1935). (6) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938). (7) Whitmore, Badertscher, *J. Am. Chem. Soc.* 55, 1561 (1933). (8) Butlerow, *Bull. soc. chim.* (2) 5, 23-24 (1866). (9) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* 61, 3107-3111 (1939).

3:7500 1-CHLORO-2,2-DIMETHYLBUTANE  $\text{CH}_3$   $\text{C}_2\text{H}_{13}\text{Cl}$  Beil. S.N. 10  
(ter-Amyl-carbinyl chloride;  
neohexyl chloride)



B.P. 116.1° at 735 mm. (1)

$n_D^{20} = 1.4200$  (1)

113.5-115° (2)

1.4190 (2)

[For prepn. of  $\bar{\text{C}}$  from 2,2-dimethylbutane (neohexane) (1:8510) with  $\text{Cl}_2$  in the cold see (2).]

[ $\bar{\text{C}}$  with Na yields (1) a mixt. of 4 compounds: 11.8% 1,1,2-trimethylcyclopropane, b.p. 50.5-57° at 735 mm.,  $D_4^{20} = 0.6907$ ,  $n_D^{20} = 1.3880$ ; 7.8% 2,2-dimethylbutene-3 (ter-butyl-ethylene) (1:8225); 27.1% 2,2-dimethylbutane (neohexane) (1:8510); and 4.3% normal coupling prod., 3,3,6,6-tetramethyloctane, b.p. 125° at 140 mm.,  $n_D^{20} = 1.423$ .]

3:7590 (1) Whitmore, Carney, *J. Am. Chem. Soc.* 63, 2633-2635 (1941). (2) Whitmore, Bernstein, Mixon, *J. Am. Chem. Soc.* 60, 2539 (1938).

3:7595  $\alpha,\alpha'$ -DICHLORODIETHYL ETHER  $\text{Cl}$   $\text{C}_4\text{H}_8\text{OCl}_2$  Beil. I - 607  
(bis-( $\alpha$ -Chloroethyl) ether)



$I_1$ —

$I_2$ —

B.P. 116-117° (1) (2)

$D_4^{25} = 1.106$  (3)  $n_D^{25} = 1.4186$  (3)

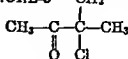
112.5-114° (3)

Colorless liq. at first immiscible with aq. but grad. hydrolyzing (especially on warming) to acetaldehyde (1:0100) and HCl (1) (2).

[For prepn. of  $\bar{\text{C}}$  from acetaldehyde (1:0100) with dry HCl gas see (2) (1).]

For identification hydrolyze  $\bar{\text{C}}$  to acetaldehyde (1:0100) (3), derivatize the latter, e.g., via the *p*-nitro- or 2,4-dinitrophenylhydrazones.

3:7595 (1) Lieben, *Ann.* 100, 337 (1858). (2) Geuther, Laatsch, *Ann.* 218, 16-18 (1883). (3) Gebauer-Fuelnegg, Moffett, *J. Am. Chem. Soc.* 56, 2009 (1934).

3:7597 2-CHLORO-2-METHYLBUTANONE-3  $\text{CH}_3$   $\text{C}_5\text{H}_9\text{OCl}$  Beil. S.N. 87

B.P. 117.2° (1)

 $D_4^{20} = 1.0083$  (1)  $n_D^{20} = 1.42044$  (1)

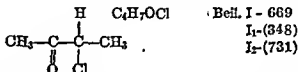
[For prepn. of  $\bar{\text{C}}$  from 2-methylbutanone-3 (isopropyl methyl ketone) (1:5410) with  $\text{SO}_2\text{Cl}_2$  in cold (84% yield (1)) or with  $\text{Cl}_2$  by vapor-phase chlorination (2) see indic. refs.]

$\bar{\text{C}}$  with 20% aq.  $\text{Na}_2\text{CO}_3$  refluxed for 37 hrs. gives (1) 2-methylbutanone-3-ol-2 [Beil. I-832, I<sub>1</sub>-(422), I<sub>2</sub>-(873)], h.p. 143° (1).

$\bar{\text{C}}$  with 40% aq.  $\text{NaOH}$  refluxed 20 hrs. gives (1) trimethylacetic acid (1:0410), h.p. 163°, m.p. 35° (1) (note structural change during this reaction).

$\bar{\text{C}}$  with aq.  $\text{KCN}$  in cold for 1 hr. gives (1) 2,3-dimethyl-2,3-epoxy-*n*-butyronitrile, h.p. 157.8° at 747 mm.,  $D_4^{20} = 0.9314$ ,  $n_D^{20} = 1.41334$  (1).

3:7597 (1) Delbaere, *Bull. soc. chim. Belg.* 51, 1-10 (1942); *Cent.* 1942, II 763-764; *C.A.* 37, 5018 (1943). (2) Justoni, *Chimica e industria (Italy)* 24, 195-201 (1942); *Cent.* 1943, I 1659.

3:7598 *d,l*-3-CHLOROBUTANONE-2  
( $\alpha$ -Chloroethyl methyl ketone)

Beil. I - 669

I<sub>1</sub>-(348)I<sub>2</sub>-(731)

B.P.

117-119° (1) at 760 mm. (8)

114-117° at 760 mm. (2)

116-117° (3)

116° at 770 mm. (4)

115° at 758 mm. (5) (15)

115° (6)

114-115° (7) (16)

114° (9)

B.P. (contd.)

49-50° at 70 mm. (6)

46° at 40 mm. (10)

32° at 40 mm. (4)

40-41° at 30 mm. (2)

33-34° at 30 mm. (7)

26° at 15 mm. (4)

 $D_4^{20} = 1.032$  (5) (15)

[See also 1-chlorobutanone-2 (3:8012).]

Liquid with penetrating odor. — Insol. aq., eas. sol. alc., ether.

[For prepn. of  $\bar{\text{C}}$  from ethyl methyl ketone (butanone-2) (1:5405) with  $\text{Cl}_2$  in pres. of  $\text{CaCO}_3$  + aq. (yields of  $\bar{\text{C}}$  about 75% always accompanied by 25% of the isomeric 1-chlorobutanone-2 (3:8012)) see (2) (6) (7) (10) cf. (11); with  $\text{Cl}_2$  as vapor-phase chlorination see (12) (13) (14); with  $\text{Cl}_2$  diluted with dry  $\text{CO}_2$  see (15) (4); with  $\text{Cl}_2$  in sunlight see (5) (16); with  $\text{SO}_2\text{Cl}_2$  in sunlight see (5) (16) (17) cf. (11); with *N*-chlorourea in dil.  $\text{AcOH}$  see (1) (8); for prepn. of  $\bar{\text{C}}$  from acetyl chloride (3:7065) with ethylene over activated carbon at 100° and 50 atm. see (18) [note that acetyl chloride + ethylene +  $\text{AlCl}_3$  at 0° gives 4-chlorobutanone-2 (3:7640) q.v.]; for prepn. of  $\bar{\text{C}}$  from 2-chlorobutene-2 (3:7105) with  $\text{Cl}_2$  + aq. +  $\text{CCl}_4$  (65% yield) see (3).]

[ $\bar{\text{C}}$  on reduction using yeast (20) gives levorotatory 3-chlorobutanol-2, h.p. 139° (cf. 3:8000), but with  $\text{Zn} + \text{HCl}$  (15)  $\bar{\text{C}}$  yields butanone-2 (1:5405).]

$\bar{\text{C}}$  on oxidn. with conc.  $\text{HNO}_3$  (5) (16) (20) yields  $\alpha$ -chloropropionic acid (3:6125).

$\bar{\text{C}}$  on hydrolysis with aq. in s.t. at 150° for 6-8 hrs. (15), or  $\bar{\text{C}}$  with alc. alk. (15) or  $\text{MeOH/KOH}$  (21) in cold, gives (84% yield (21)) butanone-2-ol-3 (acetyl-methyl-carbinol) (acetoin)

(1:5448) (as consequence of latter reactn.  $\bar{C}$  reduces Tollens' reagt. or Fehling's soln. in cold).

$\bar{C}$  with satd. aq.  $\text{NaHSO}_3$  soln. yields (15) a  $\text{NaHSO}_3$  addn. epd.

$[\bar{C}$  with conc. aq.  $\text{KCN}$  at  $0^\circ$  for 1 hr. gives (80% yield (21)) 2,3-epoxy-2-methyl-*n*-butyronitrile ( $\alpha$ -cyano- $\alpha,\beta$ -dimethyl-ethylene oxide), b.p.  $145^\circ$ ,  $D_4^{20} = 0.9540$ ,  $n_D^{20} = 1.4079$  (21);  $\bar{C}$  with alc.  $\text{KCN}$  gives (21) a mixt. consisting mainly of the above prod. together with a little  $\alpha$ -methylacetoacetonitrile [Beil. III-2 (433)], b.p.  $182$ – $184^\circ$  at 745 mm. with slight decompn. (22), h.p.  $78^\circ$  at 19 mm. (22),  $68$ – $70^\circ$  at 12 mm. (23). (Note that the above represents a correction of the earlier views (5) (16) (24).)]

$[\bar{C}$  with conc. aq.  $(\text{NH}_4)_2\text{SO}_3$  at  $70^\circ$  yields (9) butanone-2-sulfonic acid-3.— $\bar{C}$  with  $\text{NaN}_3$  in aq. contg.  $\text{AcOH}$  yields (10) 3-azidobutanone-2, oil, h.p.  $46^\circ$  at 2 mm.]

$[\bar{C}$  with  $\text{Na}$  in abs. ether gives (15) by bimolecular coupling 3,4-dimethylhexanedione-2,5 [Beil. I-798, I-2 (409), I-2 (847)], b.p.  $210^\circ$  (15),  $82^\circ$  at 11 mm.; note therefore that sodium must not be used for drying  $\bar{C}$  cf. (24).]

$[\bar{C}$  with triethyl orthoformate (1:3241) in abs. alc. in pres. of  $\text{NH}_4\text{Cl}$  as cat. gives (70% yield in 10 days but in absence of  $\text{NH}_4\text{Cl}$  only 30% (24))  $\alpha$ -chloroethyl methyl ketone diethylacetal, h.p.  $80$ – $84^\circ$  at 36 mm.,  $D_4^{20} = 0.9773$  (24).]

$[\bar{C}$  with ethyl sodio-acetoacetate in abs. ether (4) or abs. alc. (25) (26) (24) gives (yields: 45–60% (24), 27–28% (26)) the expected ethyl  $\alpha,\beta$ -diaceto-*n*-butyrate [Beil. III-757, III-2 (265), III-2 (468)], h.p.  $150^\circ$  at 28 mm. (25),  $121$ – $124^\circ$  at 11 mm. (26). —  $\bar{C}$  with ethyl acetoacetate (1:1710) + aq.  $\text{NH}_4\text{OH}$  +  $\text{NH}_3$  gas htd. for 1 hr. gives (26% yield (4)) 3-carbomethoxy-2,4,5-trimethylpyrrole [Beil. XXII-31, XXII-1 (497)], yel. cryst. from alc. or pet. eth., m.p.  $101.5$ – $102.5^\circ$  (4),  $104$ – $105^\circ$  (27), also obtd. from the above ethyl  $\alpha,\beta$ -diaceto-*n*-butyrate with conc. aq.  $\text{NH}_4\text{OH}$  on warming (4). —  $\bar{C}$  with methyl acetoacetate (1:1705) + conc. aq.  $\text{NH}_4\text{OH}$  in the cold gives (4) methyl  $\beta$ -aminocrotonate, m.p.  $82$ – $84^\circ$  (4), which only on htg. condenses with the ester to give 3-carbomethoxy-2,4,5-trimethylpyrrole [Beil. XXII-31], cryst. from dil. alc., m.p.  $124.5$ – $126^\circ$  (4) —  $\bar{C}$  with methyl acetoacetate (1:1705) +  $\text{CH}_3\text{NH}_2$  (33% in aq.) refluxed for some hours gives only very small yield (28) of 3-carbomethoxy-1,2,4,5-tetramethylpyrrole, cryst. from lgr., m.p.  $101^\circ$  (28).]

$[\bar{C}$  with diethyl acenedicarboxylate (1:1772) in dry ether at  $-15^\circ$  treated with  $\text{NH}_3$  gas gives (10.7% yield (29)) 2-carbomethoxymethyl-3-carbomethoxy-4,5-dimethylfuran, b.p.  $110$ – $115^\circ$  at 0.2 mm. (29).]

[For condens. of  $\bar{C}$  with various phenols and phenol ethers see (30).]

$[\bar{C}$  with alc.  $\text{NH}_3$  gives (15) in the cold the difficultly isolatable 3-aminobutanone [Beil. IV-319, IV-2 (452)], but on warming this condenses bimolecularly yielding (15) (8) tetramethylpyrazine [Beil. XXIII-99, XXIII-1 (28)], nols. with  $3\text{H}_2\text{O}$  from aq., m.p.  $74$ – $77^\circ$ , but aq. lost in desic. to anhydrous prod., m.p.  $86^\circ$  (8) (corresp. picrate, m.p.  $194$ – $195^\circ$  (31)). —  $\bar{C}$  with aniline (2 moles) gives (15) on refluxing 2,3-dimethylindole [Beil. XX-319, XX-1 (130)], m.p.  $107$ – $109^\circ$  (15).]

$[\bar{C}$  with thioformamide in abs. alc. for 4 days at  $0^\circ$  gives (22% yield (17)) 4,5-dimethylthiazole, b.p.  $81$ – $83^\circ$  at 59 mm. (17) (corresp. picrate, cryst. from alc., m.p.  $186$ – $187^\circ$  (17)). —  $\bar{C}$  with  $\text{NH}_4$  dithiocarbamate in abs. alc. refluxed  $\frac{1}{2}$  hr. gives (40% yield (17)) 2-mercapto-4,5-dimethylthiazole, cryst. from  $\text{EtOAc}$ , m.p.  $163.5$ – $163.8^\circ$  (17). —  $\bar{C}$  with benzamide + powd.  $\text{CaCO}_3$  htd. at  $110$ – $120^\circ$  for 10 hrs. gives (24% yield (32)) 4,5-dimethyl-2-phenyl-oxazole [Beil. XXVII-2 (219)], m.p.  $50^\circ$ , b.p.  $128$ – $130^\circ$  at 5 mm. (32). —  $\bar{C}$  with thiobenzamide +  $\text{NaOAc}$  htd. in abs. alc. gives (65% yield (32)) 4,5-dimethyl-2-phenylthiazole, h.p.  $126$ – $128^\circ$  at 6 mm. (32).]

Ⓢ 3-Chlorobutanone-2 semicarbazone: m.p.  $143^\circ$ , or on slow htg.  $143$ – $145^\circ$  dec. (33),  $127^\circ$  (1).



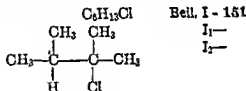
3:7598 {1} Béhal, Detoeuf, *Compt. rend.* **153**, 1230 (1911). {2} Kling, *Bull. soc. chim.* (3) **33**, 325-326 (1905); *Ann. chim.* (8) **5**, 537-539 (1905). {3} Groll, Hearne (to Shell Development Corp.), U.S. 2,060,303, Nov. 10, 1936; *Cent.* **1937**, I 4155; *C.A.* **31**, 419 (1937); *Brit.* 437,573, Nov. 28, 1935; *French* 787,529, Sept. 24, 1935; *Cent.* **1936**, II 2227. {4} Korschun, *Ber.* **38**, 1125-1129 (1905). {5} van Reymanant, *Bull. acad. roy. Belg.* **1900**, 724-742; *Cent.* **1901**, I 95. {6} Justoni, *Chimica e industria (Italy)* **24**, 89-94 (1942); *Cent.* **1943**, I 383. {7} Blaise, *Bull. soc. chim.* (4) **15**, 733 (1914). {8} Godchot, Mousseron, *Bull. soc. chim.* (4) **51**, 356 (1932). {9} Baeker, Strating, Zuithoff, *Rec. trav. chim.* **55**, 761-764 (1936). {10} Forster, Fierz, *J. Chem. Soc.* **93**, 675 (1908).

{11} Kolshorn, *Ber.* **37**, 2474-2475 (1904). {12} Justoni, *Chimica e industria (Italy)*, **24**, 195-201 (1942); *Cent.* **1943**, I 1659. {13} Calkins (to B. F. Goodrich Co.), U.S. 2,120,392, June 14, 1938; *Cent.* **1939**, I 251; *C.A.* **32**, 5854 (1938). {14} I.G., *French* 813,131, May 26, 1937; *Cent.* **1937**, II 2071. {15} Dérnètre-Vladesco, *Bull. soc. chim.* (3) **6**, 404-415, 807-829 (1891). {16} Henry, *Bull. acad. roy. Belg.* **1900**, 57-63; *Cent.* **1900**, I 1123. {17} Buchman, Reims, Sargent, *J. Org. Chem.* **6**, 767-769 (1941). {18} Frolich, Wiezevich (to Standard Oil Dev. Co.), U.S. 2,006,198, June 25, 1935, *Cent.* **1936**, I 2827; *C.A.* **29**, 5457 (1935). {19} Santomauro, *Biochem.* **7**, 171.

{20} N. V. de Bataafsche Petroleum Maatschappij, *French* 711,191 (1939); *Rend. ist. lombardo sci.* **71**, 407-424 (1938); *C.A.* **34**, 3268 (1940). {21} Mohr, *J. prakt. Chem.* (2) **90**, 199-200 (1914). {22} von Braun, Rudolph, *Ber.* **67**, 1770 (1934). {23} Youtz, Perkins, *J. Am. Chem. Soc.* **51**, 3512 (Note 5); 3514 (1929). {24} Korschun, Roll, *Gazz. chim. ital.* **41**, I 188 (1911). {25} Willstätter, Clarke, *Ber.* **47**, 307 (1914). {26} Knorr, Hess, *Ber.* **44**, 2762 (1911). {27} Korschun, Roll, *Bull. soc. chim.* (4) **33**, 1107-1108 (1923). {28} Reichstein, Zschokke, Syz, *Helv. Chim. Acta* **15**, 1115-1116 (1932). {29} Curd, Robinson, *J. Chem. Soc.* **1933**, 714-720, 1178-1179.

{30} Piloty, *Ber.* **43**, 496 (1910). {31} Friedman, Sparks, Adams, *J. Am. Chem. Soc.* **59**, 2263 (1937). {32} Blaise, *Bull. soc. chim.* (4) **17**, 426 (1915).

**3:7600 2-CHLORO-2,3-DIMETHYLBUTANE**  
(Dimethyl-isopropyl-carbinyl chloride)



**B.P. 118°** (1)

**117-119°** (2)

**112° at 749 mm.** (3)

**68° at 185 mm.** (6)

**D<sub>25</sub><sup>20</sup> = 0.8769** (2)

**D<sub>20</sub><sup>19</sup> = 0.8784** (3)

③ 2,3-Dibromo-2,3-dimethylbutane: m.p. 173-174° cor. (6), 166-168° (8). [From  $\tilde{C}$  with Br<sub>2</sub> (6).]

3:7600 (1) Silva, *Ber.* 7, 953 (1874); *Ber.* 6, 36 (1873). (2) Aschan, *Ber.* 31, 1802 (1898). (3) Pavlov, *Ann.* 196, 124 (1879). (4) Henry, *Rec. trav. chim.* 25, 147 (1906). (5) Whitmore, Rothrock, *J. Am. Chem. Soc.* 55, 1107-1108 (1933). (6) Bartlett, Condon, Schneider, *J. Am. Chem. Soc.* 66, 1533, 1537 (1944). (7) Whitmore, Laughlin, *J. Am. Chem. Soc.* 55, 3735 (1933). (8) Grosse, Ipatieff, *J. Org. Chem.* 8, 440-441 (1943).

3:7603 *d,l*- $\alpha$ -METHYL-*n*-BUTYRYL CHLORIDE  $\text{C}_5\text{H}_9\text{OCl}$  Beil. II - 306  
(Ethyl-methyl-acetyl chloride)  

$$\begin{array}{c} \text{H} \\ | \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{C}=\text{O} \\ | \quad | \\ \text{CH}_3 \quad \text{Cl} \end{array}$$

$$\begin{array}{l} \text{II}_1- \\ \text{II}_2-(270) \end{array}$$

B.P. 118.0-118.3° at 761 mm. (1)  $D_4^{20} = 0.9917$  (1)  $n_D^{20} = 1.41695$  (1)  
 115.8-116.6° (2)  
 115-116° (3)

[The dextrorotatory form of  $\tilde{C}$ , b.p. 119-120°,  $D_4^{24} = 0.990$ ,  $n_D^{17.5} = 1.4177$ , has also been reported (4).]

[For prepn. of  $\tilde{C}$  from *d,l*-2-methylbutanoic acid-1 (1:1105) with  $\text{SOCl}_2$  see (1).]

[For actn. of  $\text{PCl}_3$  on  $\tilde{C}$  see (5).]

$\tilde{C}$  with K ethyl-methyl-acetate yields (6) corresp. anhydride, b.p. 103-104° at 17 mm.

$\tilde{C}$  on hydrolysis yields *d,l*-ethyl-methyl-acetic acid (1:1105) (for the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\tilde{C}$  see 1:1105).

3:7603 (1) Lemus, *Ber.* 70, 1049 (1937). (2) Kohlrausch, Pongratz, *Z. physik. Chem. B* 22, 382 (1937). (3) Rupe, *Ann.* 369, 335 (1909). (4) Kenyon, Phillips, Pittman, *J. Chem. Soc.* 1935, 1050. (5) von Braun, Jostes, Münch, *Ann.* 453, 146-147 (1927). (6) Verkade, *Rec. trav. chim.* 36, 203 (1916).

3:7605 3-CHLORO-2,4-DIMETHYLPENTENE-2  $\text{C}_7\text{H}_{13}\text{Cl}$  Beil. I - 221  

$$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3-\text{CH}-\text{C}=\text{C}-\text{CH}_3 \\ | \\ \text{Cl} \end{array}$$

$$\begin{array}{l} \text{I}_1- \\ \text{I}_2- \end{array}$$

B.P. 118-120° (1)  $D_4^{20} = 0.9513$  (1)

[For prepn. of  $\tilde{C}$  from 2,4-dimethylpentanone-3 (di-isopropyl ketone) (isobutyron) (1:5133) with  $\text{PCl}_5$  see (1).]

$\tilde{C}$  with alc. KOH gives (1) 2,4-dimethylpentadiene-2,3 (tetramethylallene) [Beil. I-258, I<sub>1</sub>-(121)], b.p. 70° (1), 86.5° at 763 mm. [Beil. I<sub>1</sub>-(121)].

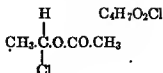
3:7605 (1) Henry, *Ber.* 8, 400 (1875).

3:7610 3,3-DICHLORO-2,4-DIMETHYLPENTANE  $\text{C}_7\text{H}_{14}\text{Cl}_2$  Beil. I - 158  

$$\begin{array}{c} \text{CH}_3 \quad \text{Cl} \quad \text{CH}_3 \\ | \quad | \quad | \\ \text{CH}_3-\text{C}-\text{C}-\text{C}-\text{CH}_3 \\ | \quad | \quad | \\ \text{H} \quad \text{Cl} \quad \text{H} \end{array}$$

$$\begin{array}{l} \text{I}_1- \\ \text{I}_2- \end{array}$$

B.P. 118-120° sl. dec. (1)  $D_4^{20} = 0.9513$  (1)

3:7625  $\alpha$ -CHLOROETHYL ACETATE $\text{C}_4\text{H}_7\text{O}_2\text{Cl}$ Beil. II - 152  
II<sub>1</sub>-(71)  
II<sub>2</sub>—

B.P. 121.5° at 746 mm. (sl. dec.) (1)

 $D_{15}^{15} = 1.114$  (1)

119-120° at 740 mm. (2)

119-121° at 740 mm. (3)

113-116° at 740 mm. (3) (4)

Note that the same observers have noted (3) two dif. b.p.'s, viz., 119-121° and 113-116° both at 740 mm., on dif. preps.; this anomaly is still unexplained.

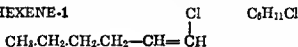
[For prepn. of  $\bar{\text{C}}$  (75% yield (5)) from paraldehyde (1:0170) +  $\text{AcCl}$  (3:7065) + trace  $\text{ZnCl}_2$  see (5) (1); from acetaldehyde (1:0100) +  $\text{AcCl}$  (3:7065) at 100° see (6); from vinyl acetate + liq. (3) or gas (7)  $\text{HCl}$  see (3) (7).]

$\bar{\text{C}}$  on htg. with 0.02%  $\text{ZnCl}_2$  at 80° yields acetaldehyde (1:0100) +  $\text{AcCl}$  (3:7065) + paraldehyde (1:0170) (8);  $\bar{\text{C}}$  passed through a tube at 360-380° or over pumice at 250-300° yields acetaldehyde + acetyl chloride (9).

$\bar{\text{C}}$  with aq. slowly hydrolyzes in cold, more rapidly on warming, yielding acetaldehyde (1:0100),  $\text{AcOH}$  (1:1010), and  $\text{HCl}$ . [This hydrolysis is accelerated by trace of acid, e.g.,  $N/10$   $\text{HCl}$  (10).]

3:7625 (1) Franchimont, *Rev. trav. chim.* 1, 245-246 (1882). (2) Descudé, *Compt. rend.* 132, 1568 (1901). (3) Gebäude-Juelnegg, Moffett, *J. Am. Chem. Soc.* 56, 2009 (1934). (4) Ulich, Adams, *J. Am. Chem. Soc.* 43, 663 (1921). (5) Colonge, Mostafavi, *Bull. soc. chim.* (5) 5, 1485-1486 (1938). (6) Simpson, *Ann.* 109, 156-157 (1859). (7) Ger. 313,696, July 19, 1919; *Cent.* 1919, IV 664. (8) Brit. 329,721, June 17, 1930; *Cent.* 1930, II 1611. (9) Brit. 330,511, July 10, 1930; *Cent.* 1930, II 2184. (10) Drushel, Bancroft, *Am. J. Sci.* (4) 44, 376 (1917).

## 3:7630 1-CHLOROHXENE-1

 $\text{C}_6\text{H}_{11}\text{Cl}$ 

Beil. S.N. 11

B.P. 121-121.5° (1)

 $D_D^{22} = 0.8872$  (1)  $n_D^{22} = 1.4300$  (1)

[For formn. of  $\bar{\text{C}}$  (together with other prods.) from either 3,3-dichloropropene-1 (3:5140) or 1,3-dichloropropene-1 (3:5280) with  $n$ -propyl  $\text{MgBr}$  see (1).]

$\bar{\text{C}}$  does not react with  $\text{NaOEt}$  at 130° (1).

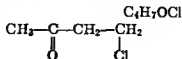
$\bar{\text{C}}$  readily reacts with  $\text{Na}$  yielding (1) hexene-1 (1:8255), b.p. 64°.

$\bar{\text{C}}$  adds  $\text{Br}_2$  yielding (1) 1,2-dibromo-1-chlorohexane, b.p. 107° at 13 mm.,  $D_D^{24} = 1.664$ ,  $n_D^{24} = 1.515$  (1).

3:7630 (1) Kirmann, Grard, *Compt. rend.* 190, 876-877 (1930); *Bull. soc. chim.* (4) 47, 843-847 (1930).

## 3:7640 4-CHLOROBUTANONE-2

( $\beta$ -Chloroethyl methyl  
ketone; 1-chlorobutanone-3)



Beil. I - 670

I<sub>1</sub>—  
I<sub>2</sub>-(731)

B.P. 120-122° at 760 mm. (1)

50-55° at 16 mm. (2)

53-55° at 15 mm. (8)

53° at 15 mm. (7)

50° at 15 mm. (3)

48-50° at 15 mm. (4)

[See also 3-chlorobutanone-2 (3:7598).]

Liquid with faint and not disagreeable odor.

[For prepn. of  $\bar{C}$  from methyl vinyl ketone [Beil. I-728, I<sub>1</sub>-(379), I<sub>2</sub>-(786)] satd. at 0° with HCl gas directly (67% yield (4)) or in  $C_6H_6$  soln. (5); from acetyl chloride (3:7065) with ethylene +  $AlCl_3$  at 0° (yields: 33% (3), 53% (6)) cf. (2) or at 100° and 50 atm. press. (22); from 4-chlorobutadiene-1,2 (3:7225) by cat. hydration with conc.  $H_2SO_4$  at -5° (yield 54% crude  $\bar{C}$  (1)); from  $\beta$ -chloropropionyl chloride (3:5690) with  $Zn(CH_3)_2$  (60% yield (7)); from hutanol-1-one-3 ( $\gamma$ -keto-*n*-butyl alcohol) by saturation with HCl gas at 0° espec. in pres. of 5-10%  $AlCl_3$  (63% yield (8)) see indic. refs.] — [Note that  $\bar{C}$  is not formed by chlorination of ethyl methyl ketone (butanone-2) (21).]

$\bar{C}$  with hot aq. alk. or alk. carbonates gives only resins, but  $\bar{C}$  on boil. with dimethyl-aniline or better diethylaniline loses HCl giving (yields: 30% and 80%, respectively (7)) methyl vinyl ketone (see above), h.p. 79-80°; note, however, that  $\bar{C}$  on warming with alc. KOH or quinoline loses both HCl and  $H_2O$  yielding (4) a mixt. of dienes, b.p. 65-75°.

[For behavior of potential  $\bar{C}$  (mixt. of methyl vinyl ketone + HCl gas in  $C_6H_6$ ) with ethylene glycol (1:6465) see (5); for reactn. of  $\bar{C}$  with trimethylene glycol (1:6490) + K yielding  $\gamma$ -hydroxypropyl  $\gamma$ -keto-*n*-butyl ether see (3).]

[ $\bar{C}$  with  $\beta$ -naphthol (1:1540) in EtOH/KOEt at 0° for 3 days gives (59% yield (9)) 1-( $\gamma$ -keto-*n*-butyl)naphthol-2, cryst. from aq. alc., m.p. 88-89° (corresp. semicarbazone, pale yel. pr. from MeOH, m.p. 179-180° (9)).]

[ $\bar{C}$  with 2-methylcyclohexanone (1:5470) in EtOH/NaOEt (or sodium isopropylate/isopropyl alc.) at 0° for 18 hrs. gives (yields: 15% (10), 10% (20)) 2-keto-10-methyl-2,3,4,5,6,7,8,10-octahydronaphthalene, h.p. 129-133° at 12 mm.,  $n_D^{25} = 1.5250$  (10).]

[ $\bar{C}$  with diethyl sodio-methylmalonate in ether gives (11) diethyl (methyl)-( $\gamma$ -keto-*n*-butyl)malonate, b.p. 114-110° at 0.4 mm.;  $\bar{C}$  with ethyl  $\alpha$ -isopropylacetacetate in EtOH/NaOEt as directed yields (13) ethyl  $\Delta$ -(1)*p*-menthene-3-carboxylate-4.]

[ $\bar{C}$  with aniline + conc. HCl or 40%  $H_2SO_4$  htd. with nitrobenzene or  $H_3AsO_4$  yields (14) (6) lepidine (4-methylquinoline) [Beil. XX-395, XXI<sub>1</sub>-(150)]; for corresp. reactn. with other amines see (14) (6).]

[ $\bar{C}$  with 1-aminoanthraquinone [Beil. XIV-177, XIV<sub>1</sub>-(436)] in pyridine yields (15) 1-( $\gamma$ -keto-*n*-butylamino)anthraquinone, dark red cryst. which dyc cellulose acetate.]

[ $\bar{C}$  with hydrazine hydrate in MeOH gives (80% yield (16)) (17) (19) by ring closure 3-methyl- $\Delta^2$ -pyrazoline [Beil. XXIII-30], liq., b.p. 56° at 15 mm. (16), sol. aq. but forming the corresp. picrate,  $\beta$  PkOH, yel. ndls. from alc., m.p. 153° (16) (17) (19). —  $\bar{C}$  in AcOH with methylhydrazine sulfate + NaOAc in aq stood 2 hrs. gives (18) 1,3-dimethyl- $\Delta^2$ -pyrazoline, oil, which with ethereal picric acid gives the corresp. picrate,  $\beta$ .PkOH, m.p. 131.5-132.5° (18). —  $\bar{C}$  with phenylhydrazine in ether gives (16) by ring closure 3-methyl-1-phenyl- $\Delta^2$ -pyrazoline, ndls. from ether by addn. of pet. ether, m.p. 76-77° (16).]

[ $\bar{C}$  with  $NH_2OH \cdot HCl$  +  $K_2CO_3$  in aq. MeOH htd. for a few minutes gives (20% yield (16)) by ring closure 3-methyl- $\Delta^2$ -isoxazoline [Beil. XXVII-12], oil, b.p. 60° at 15 mm. (16).]

③ 1-Carbamido-3-methyl- $\Delta^2$ -pyrazoline: ndls. from EtOAc, m.p. 167-168° (18), 167° (16). [Note that  $\bar{C}$  with 1 equiv. semicarbazide HCl + NaOAc in aq. immediately ppts. the corresp. semicarbazone; this on hgt. for 10 min. with strong aq. NaOAc (or  $\bar{C}$  + semicarbazide HCl + strong NaOAc soln. htd. directly in dil. alc. (19)) loses HCl and ring-closes to the indicated deriv.]

④ 1-Phenyl-3-methyl- $\Delta^2$ -pyrazoline: ndls. from ether on addn. of pet. eth., m.p. 76-77° (16), 77° (1). [From  $\bar{C}$  in ether with phenylhydrazine, followed by neutralization and drying with anhyd.  $K_2CO_3$  (16) (1); note that the presumably intermediate phenylhydrazone loses HCl and by ring closure gives the indicated deriv.]

3:7640 (1) Carothers, Berchet, Collins, *J. Am. Chem. Soc.* 54, 4070 (1932). (2) Schoeller, Zöllner (to Schering-Kahlbaum, A.G.), U.S. 1,737,203, Nov. 26, 1929, *Cent.* 1930, II 1133; Brit.

282,412, Feb. 15, 1928; *Cent.* 1929, I 143. (3) McGinnis, Robinson, *J. Chem. Soc.* 1941, 405-406. (4) Smith, Sprung, *J. Am. Chem. Soc.* 65, 1279-1280 (1932). (6) Kühn, *J. prakt. Chem.* (2) 156, 125 (1940). (6) Kenner, Statham, *Ber.* 69, 17 (1936). (7) Blaise, Maire, *Bull. soc. chim.* (4) 3, 268-270 (1908). (8) Décombe, *Compt. rend.* 202, 1685-1687 (1936). (9) McQuillin, Robinson, *J. Chem. Soc.* 1941, 588-589. (10) du Feu, McQuillin, Robinson, *J. Chem. Soc.* 1937, 53, 58-59.

(11) Lin, Robinson, *J. Chem. Soc.* 1938, 2006. (12) This reference deleted. (13) Walker, *J. Chem. Soc.* 1935, 1585. (14) Schering-Kahlbaum, A.G., *Brit.* 283,577, March 7, 1928; *Cent.* 1929, I 3148. (15) I.G., *Brit.* 485,175, June 9, 1938; *French* 828,581, May 20, 1938; *Cent.* 1938, II 3465. (16) Maire, *Bull. soc. chim.* (4) 3, 274-279 (1908). (17) Freudenberg, Stoll, *Ann.* 449, 44 (1924). (18) von Auwers, Heimke, *Ann.* 458, 205 (1927). (19) von Auwers, Ludwig, *Ber.* 69, 2348-2349 (1936). (20) Décombe, *Compt. rend.* 213, 579-581 (1941); *Cent.* 1942, II 1568.

(21) Forster, Fierz, *J. Chem. Soc.* 93, 669 (1908). (22) Frolich, Wiezevich (to Standard Oil Development Co.), U.S. 2,006,198, June 25, 1935; *Cent.* 1036, I 2827; *C.A.* 29, 5457 (1935).

3:7650 1,3-DICHLOROBUTENE-1  $\begin{array}{c} \text{Cl} \quad \quad \text{Cl} \\ | \quad \quad | \\ \text{CH}_3-\text{C}-\text{CH}=\text{CH} \\ | \\ \text{H} \end{array}$   $\text{C}_4\text{H}_6\text{Cl}_2$  Beil. S.N. 11

B.P. 120-123° (1)

$D_{20}^{20} = 1.130$  (1)

$n_D^{20} = 1.464$  (1)

Note.  $\bar{\text{C}}$  by virtue of facile allylic transposition easily isomerizes to 1,1-dichlorobutene-2 (3:7685) q.v.

[For prepn. of  $\bar{\text{C}}$  from crotonaldehyde (1:0150) with  $\text{PCl}_5$  see (1) (2); the resulting mixt. of  $\bar{\text{C}}$  with its synionic isomer (1,1-dichlorobutene-2) (supposed by (2) to have been only the latter) has been separated by very precise fractnl. distn. (1).]

$\bar{\text{C}}$  with  $\text{NaOEt}$  yields (1) 1-chloro-3-ethoxybutene-1, b.p. 132-133° at 760 mm., 54-55° at 46 mm.,  $D_{18}^{18} = 0.960$ ,  $n_D^{18} = 1.432$  (1).

$\bar{\text{C}}$  with  $\text{NaOAc}$  yields (1) 1-chloro-3-acetoxybutene-1, b.p. 57-58° at 16 mm.,  $D_{17}^{17} = 1.090$ ,  $n_D^{17} = 1.443$  (1). [Note that crotylidene diacetate (1,1-diacetoxybutene-2), prepd. (95% yield (3)) from crotonaldehyde (1:1050) with  $\text{Ac}_2\text{O}$ , gives (3) with dry  $\text{HCl}$  the isomeric 3-chloro-1-acetoxybutene-1, b.p. 64° at 13 mm.,  $D_{20}^{20} = 1.083$ ,  $n_D^{20} = 1.451$  (3).]

3:7650 (1) Kirmann, *Compt. rend.* 199, 1228-1229 (1934). (2) Kekulé, *Ann.* 162, 98-100 (1872). (3) Kirmann, *Bull. soc. chim.* (5) 5, 917-918 (1938).

3:7655 *d,l*-4-CHLOROHEXENE-1  $\begin{array}{c} \text{Cl} \\ | \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2 \\ | \\ \text{H} \end{array}$   $\text{C}_6\text{H}_{11}\text{Cl}$  Beil. I - 215  
(Allyl-ethyl-carbinyl chloride)  $\begin{array}{l} \text{I}_1- \\ \text{I}_2- \end{array}$

B.P. 120-123° dec. (1)

[For prepn. of  $\bar{\text{C}}$  from hexen-1-ol-4 (allyl-ethyl-carbinol) [Beil. I-444] with  $\text{PCl}_5$  see (1).]  $\bar{\text{C}}$  with alc.  $\text{KOH}$  yields (1) hexadiene-1,3 [Beil. I-253], b.p. 72-74°.

3:7655 (1) Fournier, *Bull. soc. chim.* (3) 15, 402, 886 (1896).

{11} Grimaux, Adam, *Bull. soc. chim.* (2) **36**, 19-21 (1881). {12} Barbaglia, *Ber.* **7**, 467-469 (1874). {13} Consortium für Elektrochem. Ind., French 707,852, July 10, 1931; *Cent.* **1931**, II 2056. {14} Akashi, *Bull. Inst. Phys.-Chem. Research (Tokyo)* **12**, 320-340 (1933); *Cent.* **1933**, I 3066; *C.A.* **27**, 3447 (1933). {15} Kling, *Bull. soc. chim.* (3) **33**, 322-323 (1905); *Ann. chim.* (8) **5**, 474-475 (1905). {16} Fritsch, *Ber.* **26**, 598 (1893); *Ann.* **279**, 315-316 (1894). {17} Malinovsky, *J. Gen. Chem. (U.S.S.R.)* **9**, 832-839 (1939); *C.A.* **34**, 375 (1940). {18} Erlenbach, *Ann.* **269**, 18-19 (1892). {19} Wislicenus, *Ber.* **43**, 3532-3533 (1910). {20} Smirnov, *J. Russ. Phys.-Chem. Soc.* **35**, 854-872 (1903); *Cent.* **1904**, I 576.

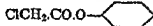
{21} Henry, *Compt. rend.* **94**, 1428 (1882). {22} Völker, *Ann.* **192**, 93-95 (1878). {23} von Romburgh, *Verslag Akad. Wetenschappen Amsterdam* **31**, 655-656 (1922); *Cent.* **1924**, I 159; *C.A.* **18**, 1271 (1924). {24} Ingold, *J. Chem. Soc.* **119**, 328-329 (1921). {25} Ingold, Sako, Thorpe, *J. Chem. Soc.* **121**, 1197 (1922). {26} Dem'yanov, Feofilaktov, *J. Gen. Chem. (U.S.S.R.)* **9**, 340-360 (1939); *Cent.* **1939**, II 2913; *C.A.* **34**, 385 (1940). {27} Winkel, Proske, *Ber.* **69**, 700-701 (1936). {28} Klumont, *Chem. Ztg.* **60**, 521 (1922). {29} Hess, Fink, *Ber.* **48**, 2001 (1915). {30} Raschig, *Pahl.* *Ber.* **59**, 2027-2028 (1926).

{31} Prjanishnikov, Leontowitsch, *Ber.* **68**, 1867 (1935). {32} Kuhn, *J. prakt. Chem.* (2) **156**, 121 (1940). {33} Rojahn, Lemme, *Arch. Pharm.* **263**, 615-616 (1925). {34} Fromm, Kapeller, Taubmann, *Ber.* **61**, 1357-1358 (1928). {35} Glattfeld, Schneider, *J. Am. Chem. Soc.* **66**, 417 (1938). {36} Fournau, *Bull. soc. chim.* (4) **29**, 413-414 (1921). {37} I.G., French 785,795, Aug. 17, 1935; *Cent.* **1936**, I 1134. {38} Hooper, Johnson, *J. Am. Chem. Soc.* **56**, 470-471 (1934). {39} Johnson (to Winthrop Chem. Co.), U.S. 2,014,493, Sept. 17, 1935; *Cent.* **1936**, I 1114; *C.A.* **29**, 7344 (1935). {40} Suter, Johnson, *Rec. trav. chim.* **49**, 1066-1068 (1930).

{41} Huntress, Pfister, *J. Am. Chem. Soc.* **65**, 1668-1670 (1943). {42} Wheeler, *J. Am. Chem. Soc.* **61**, 3654 (1929). {43} Allen, Gates, *J. Am. Chem. Soc.* **6**, 596-601 (1911).

### 3:0563 PHENYL CHLOROACETATE

$C_6H_5O_2Cl$  Beil. VI-153



VI-(87)

VI-(154)

M.P.	B.P.	
45° (1) (2)	230-235° (6)	$D_4^{25} = 1.2202$ (9) $n_D^{25} = 1.5146$ (9)
44-45° (3)	155° at 65 mm. (7)	
44° (5)	123-126° at 14 mm. (2)	
43° (7)		
40.2° (6)		

Ndls. or lfts. from alc. — Insol. aq.; eas. sol. alc., ether.

[For prepn. of  $\bar{C}$  from phenol (1:1420) with chloroacetyl chloride (3 5235) on htg. alone (7) (6) (3), in ether soln. + pyridine (2), or with  $AlCl_3$  in  $CS_2$  (1) see indie refs.; with chloroacetic acid (3:1370) +  $P_2O_5$  in  $CHCl_3$  (8) or on htg. with  $POCl_3$  or  $ZnCl_2$  (5) see (8) (5).]

$\bar{C}$  hydrolyzes rather easily, even slowly on stdg. in moist air (3)  $\bar{C}$  on mere refluxing for  $\frac{3}{4}$  hr. with abs. alc. or with alc. NaOEt undergoes trans-esterification yielding (3) ethyl chloroacetate (3:5700) and phenol (1:1420).

$\bar{C}$  in ether treated with  $NH_3$  gas reacts vigorously yielding (3)  $NH_4$  phenolate (sol. in aq.) and chloroacetamide (insol. aq.), m p. 118° (3).

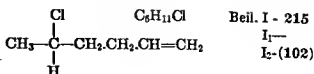
$\bar{C}$  with aniline (2 moles) at 80° for 1 hr. gives (4) aniline hydrochloride (sol. in aq.) + phenyl *N*-phenylaminoacetate [Beil. XII-471] pptd. from alc. by addn. of aq., m p. 82-83° (4). [Note that  $\bar{C}$  on boilg. with aniline yields (4) *N*-phenylaminoacetanilide (*N*-phenylglycine anilide) [Beil. XII-556], m p. 111-112° (4).]

$\bar{C}$  with phenylhydrazine (2 moles) at 50° for  $\frac{3}{4}$  hr. yields (4) phenyl  $\beta$ -phenylhydrazinoacetate [Beil. XV-321], lfts. from  $C_6H_6$  or from alc. by addn. of aq., m p. 93-94° (4).

$\bar{C}$  htd. with  $AlCl_3$  for 5 hrs. at 130-140° gives (10) *o*-hydroxyphenacyl chloride (vol. with steam), m p. 74°, + *p*-hydroxyphenacyl chloride (not vol. with steam), m p. 148°.

$\bar{C}$  + equal wt. pyridine htd. at 100° gives (1) cpd.  $\bar{C}.C_5H_5N.5H_2O$ , ndls. from alc., m p. 165-168° dec. (11), cf. (4).

**3: 7665. *d,l*-5-CHLOROHEXENE-1**  
(Biallyl hydrochloride)



B.P. 121-125° at 760 mm. (1)	$D_4^{25} = 0.8891$ (1)	$n_D^{25} = 1.4279$ (1)
120-124° (2)		
64-66° at 103 mm. (1)	$D_4^{20} = 0.9141$ (1)	$n_D^{20} = 1.4305$ (1)
43-45° at 45 mm. (1)		$n_D^{15} = 1.4332$ (1)
28-30° at 13 mm. (1)	$D_4^{12} = 0.9105$ (2)	$n_D^{12} = 1.4350$ (2)

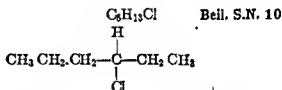
[The levorotatory isomeride of  $\bar{C}$  has also been reported (3) from dextrorotatory hexen-1-ol-5 with  $\text{PCl}_5$  in ether, h.p. 119-122° (3); ozonolysis followed by treatment with  $\text{Br}_2/\text{aq.}$  yields (3) levorotatory  $\gamma$ -chloro-*n*-valeric acid.]

[For prepn. of  $\bar{C}$  from hexadiene-1,5 (biallyl) (1:8045) by shaking at room temp. with 5 vols. conc.  $\text{HCl}$  for 120 hrs. see (1) (4) (yield of  $\bar{C}$  is 23% accompanied by 57% 1,5-dichlorohexane (3:9340) and other products (1)); for prepn. of  $\bar{C}$  from hexen-1-ol-5 (Beil. I-444) with  $\text{PCl}_5$  in  $\text{CHCl}_3$  (30% yield + much resin (2)) see (2) (attempts to obt.  $\bar{C}$  from this alc. with  $\text{HCl}$  gave (2) as a result of ring closure only 2,5-dimethyltetrahydrofuran [Beil. XVII-14], b.p. 03°).]

$\bar{C}$  on oxidn. with  $\text{CrO}_3/\text{H}_2\text{SO}_4$  for 2½ hrs. at 90-95° gave (2) formic acid (1:1005) but no allylacetone.

**3: 7665** (1) Cortese, *J. Am. Chem. Soc.* **52**, 1519-1521 (1930). (2) Courtot, Pierron, *Compt. rend.* **190**, 1057-1059 (1930). (3) Levene, Haller, *J. Biol. Chem.* **83**, 599 (1929). (4) Wurtz, *Ann. chim.* (4) **3**, 171 (1864).

**3: 7670 3-CHLOROHEXANE**  
(*sec.*-(3)-Hexyl chloride;  
ethyl-*n*-propyl-carbinyl chloride)



B.P. 123° (1)	$D_{20}^{20} = 0.870$ (2)	$n_D^{20} = 1.4163$ (2)
59.5-60° at 95 mm. (2)		

[For prepn. of  $\bar{C}$  from hexene-3 (1:8270) in  $\text{CHCl}_3$  by shaking with conc.  $\text{HCl}$  for 48 hrs. (45% yield) ( $\text{HCl}$  gas in  $\text{CHCl}_3$  fails) see (2) (for study of rate of reaction in various solvents see (4)); from hexanol-3 (1:6203) in ether +  $\text{HCl}$  gas for 5 days see (1); for formn. of  $\bar{C}$  (together with other products) from reactn. of 2-ethylbutanol-1 (1:6223) with  $\text{HCl}$  +  $\text{ZnCl}_2$  see (3).]

$\bar{C}$  with  $\text{Mg}$  in dry ether gives  $\text{RMgCl}$  which with  $\text{O}_2$  yields (3) hexanol-3 (1:6203); this alc. upon oxidn. with  $\text{CrO}_3/\text{H}_2\text{SO}_4$  yields (3) hexanone-3 (2,4-dinitrophenylhydrazone, m.p. 146.5-148.5° (3); semicarbazone, m.p. 110.5-111.5° (3)).

**3: 7670** (1) Lagerev, Shadmanov, *Trudy Uzbekskogo Gosudarst. Univ.* **6**, 89-91 (1936); *C.A.* **35**, 2120 (1941). (2) Spiegler, Tinker, *J. Am. Chem. Soc.* **61**, 942 (1939). (3) Whitmore, Karnatz, *J. Am. Chem. Soc.* **60**, 2535 (1938). (4) O'Connor, Baldinger, Vogt, Hennion, *J. Am. Chem. Soc.* **61**, 1455 (1939).

**3:7657 3-CHLORO-2-METHYL-1,2-EPOXYPROPANE**  $C_4H_7OCl$  Beil. S.N. 2362  
 ("  $\beta$ -Methylepichlorohydrin ")



B.P. 122.0° (1)

$D_4^{20} = 1.1025$  (1)

$n_D^{20} = 1.4340$  (1)

Colorless liq.;  $\bar{C}$  is sol. aq. to extent of 3 g. in 100 g. aq. at 20° (1). —  $\bar{C}$  with aq. forms a const.-boilg. mixt. (b.p. 89.8°) contg. 74.4%  $\bar{C}$  + 25.6% aq. (1).

[For prepn. of  $\bar{C}$  from 1,3-dichloropropanol-2 (dichloro-*ter*-butyl alcohol) (3:5985) with aq.  $\text{Ca}(\text{OH})_2$  (93% yield (1)) see (1) (2); from chloroacetone (3:5425) with diazomethane in ether see (3).]

$\bar{C}$  with aq. especially at elevated temps., or  $\bar{C}$  stirred for 3 hrs. at 90–95° with aq. contg. 0.1%  $\text{H}_2\text{SO}_4$  until mixt. becomes homogeneous, gives (1) (4) (by hydration through ring opening) 95% yield (1) 3-chloro-2-methylpropanediol-1,2 ( $\beta$ -methylglycerol monochlorohydrin) (3:9190). [Note that alk. also catalyzes this hydration but reacts with the prod.] [Note also that  $\text{HCl}$  may not be used since it adds to the epoxy ring yielding (3) 1,3-dichloro-2-methylpropanol-2 (3:5977).]

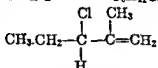
$\bar{C}$  on distn. with 12%  $\text{H}_2\text{SO}_4$  at ord. press. yields (1) (5) quant.  $\alpha$ -methylacrolein ("methacrolein") [Beil. I-731].

$\bar{C}$  with conc. aq.  $\text{NH}_4\text{OH}$  + alk. yields (1) 1,3-diamino-2-methylpropanol-2 [Beil. IV<sub>7</sub> (739)].

**3:7657** (1) Hearne, DeJong, *Ind. Eng. Chem.* **33**, 940–943 (1941). (2) Groll, Hearne (to Shell Development Co.) U.S. 2,661,277 Mar. 17, 1954; C.A. 48:1027 (1954); *Chem. Abstr.* 48:1027 (1954).

(1938).

**3:7660 *d,l*-3-CHLORO-2-METHYLPENTENE-1**  $C_6H_{11}Cl$  Beil. S.N. 11  
 ( $\alpha$ -Ethyl- $\beta$ -methylallyl chloride)



B.P. 120–124° (1)

Note.  $\bar{C}$  by virtue of allylic transposition would be expected to be in equilibrium with its isomeric isomer 1-chloro-2-methylpentene-2 ( $\gamma$ -ethyl- $\beta$ -methylallyl chloride). The material reported by (1) was regarded as  $\bar{C}$ ; the isomer appears to be as yet unrecorded.

[For prepn. of  $\bar{C}$  from 2-methylpenten-1-ol-3 by hgt. with  $\text{SOCl}_2$  + pyridine at 65° for 4 hrs. see (1).]

$\bar{C}$  in  $\text{MeOH}$  refluxed 4 hrs. with  $\text{NaSCN}$  gives (1)  $\alpha$ -ethyl- $\beta$ -methylallyl isothiocyanate, b.p. 100–200° nt 760 mm., 75–90° at 10 mm. (1). [This prod. with conc.  $\text{H}_2\text{SO}_4$  nt 0° yields 4-ethyl-5,5-dimethyl-2-mercaptothiazoline, color cryst. from alc., m.p. 115–118° (1).]

**3:7660** (1) Bruson, Eastes, *J. Am. Chem. Soc.* **59**, 1013 (1937).



Colorless liq. with not disagreeable odor.

[For prepn. of  $\bar{C}$  from butene-1 with  $Cl_2$  in aq. (5), in  $CCl_4$  (2), or at elevated temp. and press. in pres. of  $CaCl_2$  + other cat. (8) (some 1,2,3-trichlorobutane (3:5935) is also formed (5)) see indic. refs.; for prepn. of  $\bar{C}$  from 1-chlorobutane (3:7160) with  $Cl_2$  in sunlight or u.v. light (other isomers are also formed) see (9) (10) (11) (4) (7) (other isomers are always formed, and yield of  $\bar{C}$  is about 17% (7)) see indic. refs.; for formn. of  $\bar{C}$  from 2-chlorobutane (3:7125) with  $Cl_2$  in light see (6).]

[C with  $\text{Cl}_2$  at  $-17^\circ$  in dark gives (12) 1,2,3-trichlorobutane (3:5935) as main product.]

[C is not hydrolyzed by aq.  $K_2CO_3$  (6) but on htg. with excess 7-15% aq.  $NaHCO_3$  +  $Na_2CO_3$  at 135-195° under press. for 1-6 hrs. gives (13) butanediol-1,2 [Beil, I-477, I<sub>2</sub>-(545)] + 2-chlorobutene-2 (3:7105) + ethyl methyl ketone (1:5405) + mixt. of buten-1-ol-3 and buten-2-ol-1.]

$\bar{C}$  passed as vapor over heated soda-lime as directed (9) (4) (10) (11), or  $\bar{C}$  + aq. vapor at 200–500° over silica gel + cat. (14), gives (24.8% yield (9)) butadiene-1,3 (divinyl) [Beil. I-249, I<sub>1</sub>-(107), I<sub>2</sub>-(224)].

$\bar{\text{C}}$  with alc. KOH (1 mole + 25% excess) refluxed 3 days gives a mixt. contg. (2) cf. (18) 2-chlorobutene-1 (3:7075) + *cis*-1-chlorobutene-1 (3:7110) + *trans*-1-chlorobutene-1 (3:7110); note that by this method no butyne-1 is formed (15) and can be obtd. from  $\bar{\text{C}}$  + alc. KOH only by very drastic treatment, e.g., htg. in s.t. at 130–135° for 16–20 hrs. (15).]

[For reactn. of  $\bar{C}$  with phenylacetonitrile (benzyl cyanide) +  $\text{NaNH}_2$  in liq.  $\text{NH}_3$  giving (40% yield (16)) 1-cyano-2-ethyl-1-phenylcyclopropane, h.p.  $93-94^\circ$  at 1 mm.,  $D^{20}_D = 0.9921$ ,  $n^{20}_D = 1.52457$ , see (16); for condens. of  $\bar{C}$  with diphenyl ether (1:7125) +  $\text{AlCl}_3$  see (17).]

3:7680 (1) ... (1927). (2) Navez, *Bull. soc. chim. Belg.*  
39, 435-440 ... (1940). (4) Perkin,

(18) Henne, Hinkamp, *J. Am. Chem. Soc.* **67**, 1107 (1945).

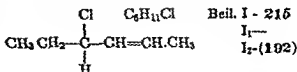
3:7685 1,1-DICHLOROBUTENE-2  $C_4H_6Cl_2$  Beil. 1-205  
(Crotylidene (di)chloride)  $CH_3-CH=CH-CHCl_2$  I<sub>1</sub>-  
I<sub>2</sub>-

B.P. 124-125° (1)  $D_4^{18} = 1.140$  (1)  $n_D^{18} = 1.466$  (1)

<sup>1</sup> C by virtue of facile allylic transposition easily isomerizes to 1,3-dichlorobutene-1 (3:7650) a.v.

[For prepn. of  $\bar{C}$  from crotonaldehyde (1:0150) with  $PCl_5$ , see (1) (2); the resulting mixt. of  $\bar{C}$  with its synionic isomer (1,3-dichlorobutene-1) (supposed by (2) to have been only  $\bar{C}$ ) has been separated by very precise fractional distn. (1).]

3:7675 *d,l*-4-CHLOROHEXENE-2  
( $\alpha$ -Ethyl- $\gamma$ -methylallyl chloride;  
 $\alpha$ -ethylcrotyl chloride)



B.P.

123-124° at 760 mm., st. dec. (1)

122-126° dec. (2) (3)

73-76° at 136 mm. (4)

66-67° at 110 mm. (5)

65-67° at 110 mm. (2)

65-70° at 110 mm. (3)

38-43° at 30 mm. (6)

30° at 13 mm. (1)

30° at 10 mm. (7)

$D_{20}^{20} = 0.9148$  (6)

$n_D^{25} = 1.4356$  (4)

$n_D^{20} = 1.4400$  (1)

1.4385 (5)

1.4382 (5)

Note. The possibility that  $\bar{C}$  may by virtue of allylic transposition exist or react in the form of its as yet unisolated synomeric isomer 2-chlorohexene-3 ( $\gamma$ -ethyl- $\alpha$ -methylallyl chloride) should not be overlooked.

[For prepn. of  $\bar{C}$  from hexen-2-ol-1 ( $\alpha$ -ethyl- $\gamma$ -methylallyl alcohol) (1) [Beil. I-445] with dry HCl gas at 0° (5) (81% yield (2)), with conc. aq. HCl (7), with PCl<sub>5</sub> (5) (6) (54% yield (8)), or with SOCl<sub>2</sub> in ether + quinoline at 0° (1) see indic. refs.]

$\bar{C}$  is readily hydrolyzed.  $\bar{C}$  on shaking with aq. at 15° is 81% hydrolyzed in 48 hrs.; 100% in 90 min. at 40° (2). —  $\bar{C}$  with 2½ pts. aq. + 1 pt. CaCO<sub>3</sub> stood 3 days gives in good yield (1) 4-chlorohexen-2-ol, b.p. 49-50° at 12 mm. (1) [acid phthalate, m.p. 52-53° (1); *p*-nitrobenzoate, m.p. 35-37° (1); *N*-(*p*-xenyl)carbamate, m.p. 102° (1)].

$\bar{C}$  on htg. in s.t. at 120° with MeOH/KOH gives (3) 4-methoxyhexene-2, b.p. 110-113° (3).

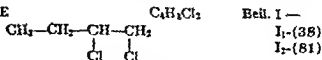
[For reactn. of  $\bar{C}$  with phenol + K<sub>2</sub>CO<sub>3</sub> in acetone see (5) (5); for extension to many phenols see (6); for reactn. of  $\bar{C}$  with diethyloxosuccinate see (4); for reactn. of  $\bar{C}$  with NH<sub>3</sub> or amines see (9) ]

$\bar{C}$  on oxida. with CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> at 40° gives (55% yield (2)) hexen-2-one-4, b.p. 137-140° (2) [2,4-dinitrophenylhydrazone, m.p. 100-101° (2)]

3:7675 (1) Aus. Balle, Kenyon, *J. Chem. Soc.* 1942, 24-26. (2) Courtot, Pierron, *Bull. soc. chim.* (4) 45, 290-291 (1929). (3) Reif, *Ber.* 39, 1603-1604 (1906), 41, 2742 (1908). (4) Shonle, Waldo, *J. Am. Chem. Soc.* 55, 4619-4632 (1933). (5) Smith, Ungrade, Lauer, Leekley, *J. Am. Chem. Soc.* 61, 3080 (1939). (6) Hurd, Puterbaugh, *J. Org. Chem.* 2, 381-386 (1937). (7) Boettcher (to I.G.), *Ger.* 513,304, Nov. 26, 1930; *Cent.* 1931, I 1007, C.A. 25, 1260 (1931). (8) Hurd, Cohen, *J. Am. Chem. Soc.* 53, 1917-1922 (1931). (9) Boettcher (to I.G.), *Ger.* 487,787, Dec. 16, 1929, *Cent.* 1930, I 1030.

3:7680 *d,l*-1,2-DICHLOROBUTANE

( $\alpha$ -Butylene dichloride)



B.P. 121.0° (1) (2) (6)

123-126° at 760 mm. (3)

abt. 125° (4)

123-125° at 768 mm. (7)

121-122° at 735 mm. (5)

31° at 28 mm. (5)

$D_4^{25} = 1.1116$  (2)

$D_4^{20} = 1.1182$  (6)

1.1187 (7)

$D_4^{15} = 1.1244$  (2)

$n_D^{20} = 1.440$  (7)

$n_D^{15} = 1.4474$  (2)

1.4472 (3)

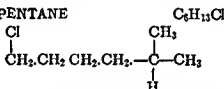
hydrazine, m.p. 108° (1)), and  $\beta$ -phenyl-*n*-butyrophenone (1,3-diphenylbutanone-1) [Beil. VII-453], m.p. 74° (1) (11). — For reactn. of  $\bar{C}$  with  $AlCl_3$  + *p*-xylene (16), mesitylene (11), acenaphthene (17), anisole (18), methyl *p*-tolyl ether (7), methyl 3,5-dimethylphenyl ether (19) see indic. refs.]

$\bar{C}$  on hydrolysis with aq. yields  $\alpha$ -crotonic acid (1:0425), m.p. 72°; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see 1:0425.

3:7693 (1) Kohler, *Am. Chem. J.* 42, 395-396 (1909). (2) Staudinger, Becker, Hirzel, *Ber.* 49, 1991 (1916). (3) Luniak, *Ber.* 42, 915-910 (1909). (4) Henry, *Bull. acad. roy. Belg.* (3) 36, 42 (1898); *Cent.* 1898, II 663. (5) Maxim, *Bul. Soc. Chim. România*, 10, 97-115 (1928); *Cent.* 1929, I 2161; *C.A.* 23, 2697 (1929). (6) Jones, Mason, *J. Am. Chem. Soc.* 40, 2533 (1927). (7) von Auwers, *Ann.* 421, 30-36 (1921). (8) Kohlrausch, Pongratz, *Z. physik. Chem.* B-27, 193 (1934). (9) von Auwers, Schmidt, *Ber.* 46, 474 (1913). (10) Kuhn, F. Köhler, L. Köhler, *Z. physiol. Chem.* 247, 197-219 (1937); *Cent.* 1937, II 2391; *C.A.* 31, 6264 (1937). (11) Fuson, Christ, Whitman, *J. Am. Chem. Soc.* 58, 2450-2452 (1936). (12) von Auwers, Spiess, *Ber.* 34, 191-192 (1901). (13) Brown, *J. Am. Chem. Soc.* 60, 1325-1328 (1938). (14) Rupe, Schaerer, *Helv. Chim. Acta* 8, 863 (1925). (15) Wedekind, *Ann.* 378, 288 (1910). (16) von Auwers, Risse, *Ann.* 502, 291-292 (1933). (17) Fieser, Herschberg, *J. Am. Chem. Soc.* 61, 1280 (1939). (18) von Auwers, *Ann.* 439, 150 (1924). (19) Ref. 7, pp. 97-100.

### 3:7695 5-CHLORO-2-METHYLPENTANE

(Isohexyl chloride)



Beil. I —

I<sub>1</sub>-(53)

I<sub>2</sub>—

B.P. 125-126° at 761 mm. (1)

[For prepn. of  $\bar{C}$  from *N*-(benzoyl)isohexylamine with  $PCl_5$  followed by aq. see (1).]

$\bar{C}$  on htg. in alc. with diethyl sodiomalonate in a s.t. at 100° for 4 hrs. gives an ester from which 2-methyloctanoic acid-8, b.p. abt. 230°, was obtd. by conventional methods (1).

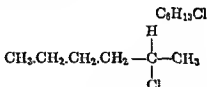
3:7695 (1) Clarke, *J. Chem. Soc.* 103, 1699 (1913).

### 3:7715 2-CHLOROHEXANE

(sec.-(2)-Hexyl

chloride; *n*-butyl-

methyl-carbinyl chloride)



Beil. I - 144

I<sub>1</sub>-(52)

I<sub>2</sub>-(109)

B.P. 125-127° (1)

123-126° (2)

122.5° at 764 mm. (3)

61° at 100 mm. (3)

$D_4^{21} = 0.8694$  (3)  $n_D^{21.5} = 1.4142$  (3)

$D_4^{14} = 0.8762$  (3)

[For prepn. of  $\bar{C}$  from corresp. alc. hexanol-2 (1:6210) with conc. HCl at 125° (90% yield (3)) or conc. HCl (1) (2) see indic. refs.; for forma. of  $\bar{C}$  (together with other products) from reaction of 2-ethylbutanol-1 (1:6223) with conc. HCl +  $ZnCl_2$  see (4).]

$\bar{C}$  on passing over Pyrex glass or unglazed porcelain at 150-500° loses HCl (5).

[For study of rate of reaction with KI in acetone see (2).]

$\bar{C}$  with Mg in dry ether gives  $RMgCl$ ; upon treatment with oxygen this gives (4) hexanol-2 (1:6210) q.v.

④ *n*-Butyl-methyl-acet-anilide: m.p. 91-92° u.c. (1). [From  $\bar{C}$  via conversion to  $RMgCl$  and reaction with phenyl isocyanate (1).]

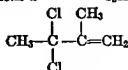
Crotylidene diacetate (from crotonaldehyde (1:0150) +  $\text{Ac}_2\text{O}$  in 95% yield (3)) gives (3) with dry  $\text{HCl}$  3-chloro-1-acetoxybutene-1, b.p.  $64^\circ$  at 13 mm.,  $D_{20}^{20} = 1.083$ ,  $n_D^{20} = 1.451$  (3), derived from the synionic isomer of  $\bar{\text{C}}$ .

3:7685 (1) Kirmann, *Compt. rend.* 199, 1228-1229 (1934). (2) Kekulé, *Ann.* 162, 98-100 (1872). (3) Kirmann, *Bull. soc. chim.* (5) 6, 917-918 (1938).

### 3:7690 3,3-DICHLORO-2-METHYLBUTENE-1

 $\text{C}_4\text{H}_5\text{Cl}_2$ 

Beil. S.N. 11



B.P.  $124-126^\circ$  at 762 mm. (1)  
 $55-57^\circ$  at 60 mm. (1)

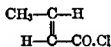
 $D_4^{10} = 1.085$  (1)  $n_D^{19} = 1.4513$  (1)

[For prepn. of  $\bar{\text{C}}$  from 3-chloro-2-methylbutene-2 (3:7335) with  $\text{Cl}_2$  +  $\text{NaHCO}_3$  at  $0^\circ$  see (1) (yield 80% together with 10% 2,3,3-trichloro-2-methylbutane (3:4755), m.p.  $182-183^\circ$  (1))]

$\bar{\text{C}}$  on htg. gives by allylic transposition 1,3-dichloro-2-methylbutene-2 (3:8170) (1).

3:7690 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, II 4223; *C.A.* 33, 4190 (1939).

### 3:7693 $\alpha$ -CROTONOYL CHLORIDE

 $\text{C}_4\text{H}_5\text{OCl}$ 

Beil. II - 411

 $\text{II}_1$ -(188) $\text{II}_2$ -(392)B.P.  $126^\circ$  (1) $D_4^{20} = 1.080$  (9) $124-126^\circ$  (2) $124-125^\circ$  at 769 mm. (3) $D_4^{20} = 1.0905$  (3) $124-125^\circ$  (4) (5) $124^\circ$  (6) $123-124^\circ$  (7) $D_4^{17.4} = 1.0822$  (9)  $n_D^{17.9} = 1.46001$  (9) $122.6-123.6^\circ$  (8) $34-36^\circ$  at 18 mm. (3)

The name crotonoyl chloride is employed to avoid possible confusion with 1-chlorobutene-2 (3:7205) often designated as crotonyl chloride because of its relationship to crotonyl alcohol (buten-2-ol-1).

[For prepn. of  $\bar{\text{C}}$  from  $\alpha$ -crotonic acid (1:0425) with  $\text{SOCl}_2$  (yield: 95% (5), 86% (11)) (6) (8) (10) in pet. ether (80% yield (2)), or with  $\text{PCl}_5$  (84% yield (3)) (7) (4), or with  $\text{PCl}_5$  (12), or with benzoyl chloride (3:6240) (yield: 72-80% (13)) see indic. refs.; for prepn. of  $\bar{\text{C}}$  from  $\text{Na}\bar{\text{A}}$  with  $\text{PCl}_5$  +  $\text{POCl}_3$  (1), with  $\text{PCl}_5$  in ether (26% yield (14)), or with  $\text{POCl}_3$  (9) see indic. refs.; for prepn. of  $\bar{\text{C}}$  by distn. of isocrotonyl chloride see (12).]

$\bar{\text{C}}$  with  $\text{EtOH}$  yields (4) (by addn. of the resultant  $\text{HCl}$ ) ethyl  $\beta$ -chloro- $n$ -butyrate (3:8373).

[ $\bar{\text{C}}$  on htg with  $\text{Na}\bar{\text{A}}$  (3) or with  $\text{Et}_3\text{N}$  +  $\text{C}_6\text{H}_6$  in the cold (15) gives (81% yield (3)) crotonic anhydride (1:1155), h p.  $248^\circ$ .]

[For reactn. of  $\bar{\text{C}}$  with methyl diazoacetate see (2), with  $\text{NaN}_3$  see (6).]

[ $\bar{\text{C}}$  with  $\text{AlCl}_3$  +  $\text{C}_6\text{H}_6$  in  $\text{CS}_2$  in light gives (61% yield (11)) (1) both phenyl propenyl ketone [Beil. VII-368, VII-(194)], h.p.  $135-140^\circ$  at 20 mm. (1),  $90-95^\circ$  at 2 mm. (11),  $n_D^{20} = 1.5475$  (11) (corresp. 1,3-diphenyl-5-methylpyrazoline from ketone with phenyl-

3:7735 3-CHLOROHEXATETRAENE-1,3,4,5  $\text{Cl}$   $\text{C}_6\text{H}_5\text{Cl}$  Beil. S.N. 14



B.P. 127° dec. at 760 mm. (1)

$D_4^{20} = 0.9997$  (1)  $n_D^{20} = 1.5280$  (1)

82° at 163 mm. (1)

55° at 54 mm. (1)

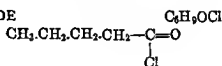
[For prepn. of  $\bar{\text{C}}$  from 1,4-dichlorohexatriene-2,3,5 (3:9304) with MeOH/KOH at 10-15° or with NaOMe in dry MeOH see (1).]

$\bar{\text{C}}$  on cat. hydrogenation yields (1) *n*-hexane (1:8530).

$\bar{\text{C}}$  on oxidn. with aq.  $\text{KMnO}_4 + \text{Na}_2\text{CO}_3$  soln. for 10 hrs. at 35-45° gives (1) oxalic acid dihydrate (1:0445).

3:7735 (1) Coffman, Carothers, *J. Am. Chem. Soc.* 55, 2040-2047 (1933).

3:7740 *n*-VALERYL CHLORIDE



Beil. II - 301

II<sub>1</sub>-

II<sub>2</sub>-(266)

B.P.

127-128°

(1) F.P. -110.0° (2)  $D_4^{20} = 1.0004$  (3)  $n_D^{20} = 1.4207$  (3)

127.2°

(2)

1.4200 (4)

126.9° at 756 mm. (3)

126° at 730 mm. (4)

124.8-126.8° (5)

125-127° (6)

123-127° (7)

[For prepn. of  $\bar{\text{C}}$  from *n*-valeric acid (1:1060) with  $\text{PCl}_5$  (60% yield (8)), with  $\text{PCl}_5$  (77% yield (9)) (1) or  $\text{PCl}_5 + \text{ZnCl}_2$  (75% yield (8)), with  $\text{SOCl}_2$  (yield: 92.5% (7), 84% (4), 77% (8)), with benzoyl chloride (3:6240) (84-76% yield (6)), or with oxalyl dichloride (3:5060) (95% yield (10)) see indic. refs.]

$\bar{\text{C}}$  htd. with sodium *n*-valerate yields (11) *n*-valeric anhydride (1:1137), b.p. 218°.

[ $\bar{\text{C}}$  with  $\text{EtMgBr}$  gives (66% yield (4)) 3-ethylheptanol-3;  $\bar{\text{C}} + \text{AlCl}_3$  treated at 0° with ethylene gives (74% yield (12)) (13) *n*-butyl  $\beta$ -chloroethyl ketone (1-chloro-heptanone-3), but its constants have not been reported.]

[ $\bar{\text{C}}$  with  $\text{AlCl}_3$  and phenol yields (14) 56% *o*-(*n*-valeroyl)phenol, h.p. 130° at 10 mm.,  $D_4^{24} = 1.0435$ ,  $n_D^{25.5} = 1.5309$  (semicarbazone, m.p. 204-204.5°), and 29% *p*-(*n*-valeroyl)phenol, cryst. from pet. ether, m.p. 63°, b.p. 197.5-198.5° at 10 mm. (benzoate, m.p. 92°).]

$\bar{\text{C}}$  on hydrolysis yields *n*-valeric acid (1:1060), b.p. 186°. — For the amide, anilide, *p*-toluidide,  $\alpha$ -naphthalide, and other derivs. corresp. to  $\bar{\text{C}}$  see *n*-valeric acid (1:1060).

(1) Pickard, Kenyon, *J. Chem. Soc.* 1912, 1432 Note (1912). (2) Timmermans, *J. Chem. Soc.* 1936, 162. (4) Ohlrausch, Pongratz, *Z. physik.* 1328 (1938). (7) Fierz-David, *v. Roy. Soc. Can.* III 27, 97-103 (1938). (11) Adams, *J. Am. Chem. Soc.* 61, 833 (1895).

(12) Kenner, Statham, *Ber.* 69, 17 (1936). (13) Schering-Kahlbaum Akt. Ges., Brit. 282,412, Feb. 15, 1928; *Cent.* 1929, I 143. (14) Sandulesco, Girard, *Bull. soc. chim.* (4) 47, 1308-1309 (1930).

3:7715 (1) Underwood, Gale, *J. Am. Chem. Soc.* 50, 2119 (1934). (2) Conant, Hussey, *J. Am. Chem. Soc.* 47, 485 (1925). (3) Zelinskii, Przewalskii, *J. Russ. Phys.-Chem. Soc.* 40, 1105-1123 (1908); *Cent.* 1908, I 1854. (4) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938). (5) Farragher, Garner, *J. Am. Chem. Soc.* 43, 1721 (1921).

3:7720 2-ETHYLBUTYL CHLORIDE  $\text{C}_6\text{H}_{13}\text{Cl}$  Beil. S.N. 10  
(1-Chloro-2-ethylbutane;  
3-(chloromethyl)pentane)  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{Cl}$

B.P. 125-127° (1)  
88° at 225 mm. (2)

$D_4^{20} = 0.8914$  (2)  $n_D^{20} = 1.4230$  (2)

[For prepn. of  $\hat{\text{C}}$  from 2-ethylbutanol-1 (1:6223) with  $\text{SOCl}_2$  + pyridine (82% yield) see (2); with 45%  $\text{HCl}$  in a.t. at 100° (11% yield) see (1).] [Note that 2-ethylbutanol (1:6223) with conc.  $\text{HCl}$  +  $\text{ZnCl}_2$  gives (2) by rearr. of the carbon chain 7 different chlorohexanes.]

$\hat{\text{C}}$  on shaking at 79-87° for 7 hrs. with conc.  $\text{HCl}$  +  $\text{ZnCl}_2$  rearranges in part to a mixt. of other hexyl halides (2).

$\hat{\text{C}}$  with  $\text{Mg}$  in dry ether gives  $\text{RMgCl}$ ; upon treatment with oxygen this yields (2) 2-ethylbutanol-1 (1:6223) q.v.

$\Phi$   $\beta$ -Ethylvaleraniide: m.p. 83-84° (2) [From  $\hat{\text{C}}$  via conversion to  $\text{RMgCl}$  and reaction with phenyl isocyanate; so prepared, m.p. 80.5-81.5° (2).]

3:7720 (1) Fournesau, Matti, *J. pharm. chim.* (6) 14, 513-522 (1931), *Cent.* 1932, I 2587. (2) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2533-2536 (1938).

3:7725 d,l-4-CHLORO-2,4-DIMETHYLPENTENE-1  $\text{C}_7\text{H}_{13}\text{Cl}$  Beil. I - 220  
 $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)\text{Cl}$   
I<sub>1</sub>—  
I<sub>2</sub>—

B.P. 126-128° (1)  
45-48° at 40 mm. (1)

[For prepn. of  $\hat{\text{C}}$  from ethyl  $\beta$ -chloroisovalerate +  $\text{MeMgBr}$  in ether see (1).]

3:7725 (1) Lemaire, *Bull. acad. roy. Belg.* 1902, 83-159; *Cent.* 1902, I 1952; *C.A.* 4, 1483-1484 (1910), *Rec. trav. chim.* 29, 51-52 (1910).

3:7730 d,l-4-CHLORO-5-METHYLHEXENE-1  $\text{C}_7\text{H}_{13}\text{Cl}$  Beil. I - 220  
d,l-3-Chloro-2-methylhexene-5  
(Allyl-isopropyl-carbinyl  
chloride)  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{C}(\text{CH}_3)(\text{Cl})-\text{CH}_2-\text{CH}_3$   
I<sub>1</sub>—  
I<sub>2</sub>—

B.P. 125-130° dec. (1)

[For prepn. of  $\hat{\text{C}}$  from 2-methylhexen-3-ol-3 (allyl-isopropyl-carbinol) [Beil. I-447] with  $\text{PCl}_5$  see (1).]

3:7730 (1) Fournier, *Bull. soc. chim.* (3) 13, 656 (1896).

$\bar{C}$  on htg. in s.t. at 140–160° yields (29) 1,2-dichloropropane (3:5200) + acetone (1:5400);  $\bar{C}$  similarly htd. with aq. yields (29) acetone (1:5400) + propionaldehyde (1:0110). —  $\bar{C}$  on htg. with  $P_2O_5$  yields (5) allyl chloride (3:7035) + 1-chloropropene-1 (3:7035).

$\bar{C}$  with aq. alk. readily gives (30) by loss of HCl and ring closure 1,2-epoxypropene (propylene oxide) (1:6115), b.p. 35°. [For study of rate of reactn. see (10) (31).]

$\bar{C}$  on oxidn. with  $CrO_3$  yields (17) (14) (18) (5) (7) chloroacetone (3:5425) + AcOH (1:1010);  $\bar{C}$  treated with  $Ca(OC_2H_5)_2$  in cold, then warmed, yields (32) chloroform (3:5050) + AcOH (1:1010);  $\bar{C}$  on oxidn. with  $HNO_3$  yields chloroacetic acid (3:1370) + AcOH (1:1010) + oxalic acid (1:0445).

[For reactn. of  $\bar{C}$  with  $Na_2S$  yielding (9) (33)  $\beta,\beta'$ -dihydroxy-di-*n*-propyl sulfide; with  $Me_3N$  in  $C_6H_6$  on htg. in s.t. 8 hrs. at 100° giving (48% yield (34))  $\beta$ -methylethanolamine chloride, m.p. 165° (34); with alkyl sulfates + alk. (35) to yield monoalkyl ethers of propylene glycol; with alkyl sulfates to yield (35) (36)  $\beta$ -chloroisopropyl alkyl ethers; with  $Br_2$  + P to yield (8) 1-bromo-2-chloropropane, b.p. 117.5–118° at 756 mm.,  $D_4^{20} = 1.537$ ,  $n_D^{20} = 1.47447$  (8), see indic. refs.]

—  $\beta$ -Chloroisopropyl acetate: b.p. 149–150° (3) (2). [From  $\bar{C}$  + AcCl (3).]

—  $\beta$ -Chloroisopropyl benzoate: no b.p. recorded;  $D_4^{19} = 1.172$  (14). [From  $\bar{C}$  on htg. with  $BzCl$  nt 180° (14); is saponified with great ease by alk. yielding propylene oxide (1:6115), b.p. 35°.]

—  $\beta$ -Chloroisopropyl  $\beta$ -nitrobenzoate: unreported.

①  $\beta$ -Chloroisopropyl 3,5-dinitrobenzoate: m.p. 76.5–77.3° (38).

② 1-(Phthalimido)propanol-2 [*N*-( $\beta$ -hydroxy-*n*-propyl)phthalimide: m.p. 88–89° (39), 90–91° (40). [From  $\bar{C}$  + K phthalimide in s.t. at 170° for 3 hrs. (39); see also under corresp. deriv. of 2-chloropropanol-1 (3:7917).]

3:7747 (1) Dewael, *Bull. soc. chim. Belg.* **33**, 504 (1924). (2) Henry, *Rec. trav. chim.* **22**, 209–210, 326–329 (1903). (3) Bancroft, *J. Am. Chem. Soc.* **41**, 426–427 (1919). (4) Henry, *Bull. acad. roy. Belg.* **1902**, 535–536; *Cent.* **1902**, II 1093–1094. (5) Michael, *Ber.* **39**, 2786–2789 (1906). (6) Meerwein, Hinz, Majert, Sönke, *J. prakt. Chem.* (2) **147**, 237 (1936). (7) Henry, *Bull. acad. roy. Belg.* **1903**, 397–431; *Cent.* **1903**, II 486. (8) Dewael, *Bull. soc. chim. Belg.* **39**, 87–90 (1930). (9) Coffey, *J. Chem. Soc.* **119**, 96–97 (1921). (10) Smith, *Z. physik. Chem.* **93**, 59–85 (1919).

(11) Oppenheim, *Ann. Suppl.* **6**, 367–369 (1868). (12) Michael, *J. prakt. Chem.* (2) **60**, 420–423 (1899). (13) Oser, *Ann. Suppl.* **1**, 254 (1861). (14) Morley, Green, *J. Chem. Soc.* **47**, 227, Jan. 8, 1935; *Cent.* **1935**, II 350; *C.A.* **29**, 1432–252 (1870). (15) Michael, *J. prakt. Chem.* (2) **3**, Canadian **285,920**, Dec. 25, 1928; *Cent.* **1932**, I 1153. (20) Tropsch, Kassler, *Brit.* **377,595**, Aug. 18, 1932; *Cent.* **1932**, II 2724.

(21) Henry, *Rec. trav. chim.* **26**, 138 (1907); *Bull. acad. roy. Belg.* **1906**, 523–557; *Cent.* **1906**, II 1550–1551. (22) Britton, Nutting, Huscher (to Dow Chem. Co.), U.S. **2,130,226**, Sept. 13, 1938; *Chem. Abstr.* **32**, 1055, Apr. 24, 1938. (23) Smith, *Phys.* **5**, 2053, Apr. 24, 1938. (24) Kaplan, *Phys.* **5**, 1918, Apr. 24, 1938. (25) Davidson, *C.A.* **23**, 12 (1935). (26) Kaplan, *Phys.* **5**, 17 (1917).

(27) Smith, *Z. physik. Chem.* **A-152**, 153–156 (1931). (32) Ssuknewitsch, Tschilingarjan, *Ber.* **69**, 1542 (1936). (33) Farhwerke Meister, Lucius Brüning, *Brit.* **185,403**, Oct. 25, 1922; *Chem. Abstr.* **17**, 1055, Apr. 24, 1923. (34) Davidson, *C.A.* **23**, 12 (1935). (35) Davidson, *C.A.* **23**, 12 (1935). (36) Kaplan, *Phys.* **5**, 17 (1917).

281–295 (1937). (31) Smith, *Z. physik. Chem.* **A-152**, 153–156 (1931). (32) Ssuknewitsch, Tschilingarjan, *Ber.* **69**, 1542 (1936). (33) Farhwerke Meister, Lucius Brüning, *Brit.* **185,403**, Oct. 25, 1922; *Chem. Abstr.* **17**, 1055, Apr. 24, 1923. (34) Davidson, *C.A.* **23**, 12 (1935). (35) Davidson, *C.A.* **23**, 12 (1935). (36) Kaplan, *Phys.* **5**, 17 (1917).

(37) Smith, *Z. physik. Chem.* **A-152**, 153–156 (1931). (32) Ssuknewitsch, Tschilingarjan, *Ber.* **69**, 1542 (1936). (33) Farhwerke Meister, Lucius Brüning, *Brit.* **185,403**, Oct. 25, 1922; *Chem. Abstr.* **17**, 1055, Apr. 24, 1923. (34) Davidson, *C.A.* **23**, 12 (1935). (35) Davidson, *C.A.* **23**, 12 (1935). (36) Kaplan, *Phys.* **5**, 17 (1917).

## 3:7745 ETHOXYACETYL CHLORIDE



Boll. III - 210

III<sub>1</sub>-(92)III<sub>2</sub>-(173)

B.P. 127-128° (1) (2)

 $D_4^{25} = 1.1170$  (4)  $n_D^{25} = 1.42030$  (4)

123-121° (3)

49-50° at 37 mm. (4)

Colorless limpid liq. with strong odor and lachrymatory character; fumes in moist air.

[For prepn. from ethoxyacetic ac. (1, 1070) by actn. of  $\text{PCl}_5$  (90% yield (2)) see (1) (2); by actn. of thionyl chloride (90% yield (5), 73% yield (3), 45% yield (4)) see (3) (4) (5) (6)]

$\bar{C}$  in aq. sinks to bottom in oily drops which soon dissolve by hydrolysis to ethoxyacetic acid (1:1070) +  $\text{HCl}$ .

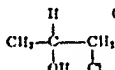
3:7745 (1) Henry, *Rev.* 2, 276-277 (1869). (2) Pratt, Robinson, *J. Chem. Soc.* 123, 752, footnote (1921). (3) Rothstein, *Bull. soc. chim.* (4) 81, 541-542 (1912). (4) Leimu, *Ber.* 36, 1050 (1917). (5) Bergetlet, *Ann. chim.* (8) 9, 492-493 (1906); *Bull. soc. chim.* (4) 1, 365-369 (1907). (6) Jones, Pinner, *J. Am. Chem. Soc.* 46, 2525 (1924).

3:7747 *d,l*-1-CHLOROPROPANOL-2

Boll. I - 363

(Propylene  $\alpha$ -chlorohydrin; $\beta$ -chloromethylpropyl alcohol;

chloromethyl-methyl-carbinol)

I<sub>1</sub>-(185)I<sub>2</sub>-(383)

B.P.

127-128° at 761 mm. (1) (14)

 $D_4^{25} = 1.115$  (1)  $n_D^{25} = 1.43024$  (2)

127° (13)

1.111 (2)

126-127° cor. at 763 mm. (2) (3) (21)

126-127° at 760 mm. (4)

126.0-126.5° cor. at 722 mm. (5)

78-81° at 80 mm. (6)

[See also 2-chloropropanol-1 (3:7917)]

Colorless liq. forming with aq. a turbid, opaq. mixt., b.p. 96° at 743 mm., contg. 49.1 wt.  $\bar{C}$  = 15.15 mole %  $\bar{C}$  (17).

[For prepn. of  $\bar{C}$  from allyl chloride (3:7025) by addn. of  $\text{H}_2\text{O}$  to the unsatd. linkage through the actn. of  $\text{H}_2\text{SO}_4$  +  $\text{CaSO}_4$  as specified (yield 66-70% (8)) (9) (3) (5) (2) (11) see infra. refs.; an extensive study (10) has shown that this is the only method of prepn. of  $\bar{C}$  which does not give also some 2-chloropropanol-1 (propylene  $\beta$ -chlorohydrin (3:7917))]

[For prepn. of  $\bar{C}$  and  $\bar{C}$  (probably containing some of the isomer) from propenol-1, 2 (propylene glycol) (1:6425) with  $\text{HCl}$  (2) (12) (10), with  $\text{SbCl}_3$  (14) (16), or with  $\text{SnCl}_4$  (15) see infra. refs.; from propylene glycol carbonate with an alc. +  $\text{HCl}$  see (16); from propylene with  $\text{HNO}_3$  (17) (18) (19) (20) (10) (21), with  $\text{Cl}_2$  + aq. (22) (23) (20), or with  $\alpha$ -butyl hypochlorite (3:7167) (24) see infra. refs.; from 1,2-epoxypropene (propylene oxide) (1:6415) with  $\text{HCl}$  see (17) (1) (2) (7) (25) (10), note, however, that by these methods there results an impure mixt. of  $\bar{C}$  with a little 2-chloropropanol-1 (3:7917) (17)]

[For prepn. of  $\bar{C}$  from allyl carbonate (1:6425) with  $\text{AlHCl}_2$  ethoxide (70% yield (1)) or by actn. of  $\text{NaOH}$  (26), from 2-amino-1,3-dioxepane with nitrous acid (27) or from 1,2-dithio- $\alpha$ -propene (propylene dithiol-1) (3:2761) with  $\text{SnCl}_4$  followed by hydrolysis (28) see infra. refs.]



3:0565 (1) Kuncell, Johannssen, *Ber.* 30, 1714-1715 (1897). (2) Mannich, Drauzburg, *Arch. Pharm.* 250, 534 (1912). (3) Morel, *Bull. soc. chim.* (3) 21, 958-964 (1899). (4) Morel, *Bull. soc. chim.* (3) 21, 964-966 (1899). (5) Nencki, *Ber.* 26, Ref., 588 (1893). (6) Prevost, *J. prakt. Chem.* (2) 4, 379-380 (1871). (7) Fries, Pfaffendorf, *Ber.* 43, 214-215 (1910). (8) Bakunin, *Gazz. chim. ital.* 30, II 358 (1900). (9) van der Stichele, *J. Chem. Soc.* 123, 1228 (1923). (10) von Auwers, Mauss, *Ber.* 61, 419 (1928). (11) Barnett, Cook, *J. Chem. Soc.* 121, 797 (1922).

3:0572 DI-( $\beta$ -CHLOROETHYL) OXALATE  $C_6H_8O_4Cl_2$  Beil. S.N. 170  
 $CO.O.CH_2.CH_2Cl$   
 $CO.O.CH_2.CH_2Cl$


M.P. 45° (1) B.P. 132° at 3 mm. (2)

[For prepn. of  $\bar{C}$  from ethylene chlorohydrin (3:5552) with anhydrous oxalic acid (1:0535) by satn. with HCl gas and htg. at 100° see (1).]

[ $\bar{C}$  with  $Me_3N$  in  $C_6H_6$  gives (1) "oxalyleholine chloride,"  $C_{12}H_{26}O_4N_2Cl_2$ , very hygroscopic cryst. ndls. (chloraurate, m.p. 256.5° dec.).]

[ $\bar{C}$  +  $C_6H_6$  +  $AlCl_3$  gives (2) bibenzyl (1:7149) + tar.]

3:0572 (1) Contardi, Ercoli, *Atti IX congresso intern. chim. Madrid* 9, V, 163-173 (1934); *Cent.* 1036, II 3903-3904; *C.A.* 31, 1764 (1937). (2) Markarov-Zemlyanskii, Korshak, Savenkov, *J. Gen. Chem. (U.S.S.R.)* 11, 331-334 (1941); *Cent.* 1942, 1 993; *C.A.* 35, 5883 (1941).

3:0580 3,4,5-TRICHLOROTOLUENE  $CH_3$   $C_7H_5Cl_3$  Beil. V - 299  
  
 $V_1-$   
 $V_2-$

M.P. 44.5-45.5° (1) B.P. 245.5-247° at 768 mm. (2)  
 42.5° (2)

Readily volatile with steam.

[For prepn. of  $\bar{C}$  from 3,5-dichloro-4-aminotoluene [Beil. XII-990] or from 4,5-dichloro-3-aminotoluene [Beil. XII-872] via diazotization and use of  $Cu_2Cl_2$  reactn. see (1); from potassium salt of 3,4,5-trichlorotoluenesulfonic acid-2 by hydrolysis with strong  $H_2SO_4$  see (2).]

[ $\bar{C}$  with  $Cl_2$  in pres. of  $Al/Hg$  yields (3) 2,3,4,5-tetrachlorotoluene (3:2710), m.p. 97-98° (3).]

$\bar{C}$  on mononitration with cold fuming  $HNO_3$  (1) yields 3,4,5-trichloro-2-nitrotoluene [Beil. V-333], pr. from alc., m.p. 81-82° (1);  $\bar{C}$  on dinitration with a mixt. of 6 pts. fuming  $HNO_3$  and 4 pts. conc.  $H_2SO_4$  (1) yields 3,4,5-trichloro-2,6-dinitrotoluene [Beil. V-346], ndls. from  $AcOH$ , m.p. 163-164° (1).

$\bar{C}$  on oxidn. with dil  $HNO_3$  in s.t. at 130° readily yields (1) 3,4,5-trichlorobenzoic acid (3:4920), m.p. 203° (1).

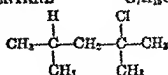
3:0580 (1) Cohen, Dakin, *J. Chem. Soc.* 81, 1330-1339 (1902). (2) Wynne, *J. Chem. Soc.* 61, 1970-1971 (1892). (3) Cohen, Dakin, *J. Chem. Soc.* 89, 1454 (1906).

## 3: 7750 2-CHLORO-2,4-DIMETHYLPENTANE

(Dimethyl-isobutyl-carbinyl chloride)



Beil. I -

I<sub>1</sub>-(59)I<sub>2</sub>-

B.P. 127-128° dec. at 733 mm. (1)

126-127° (2)

33-34° at 20 mm. (3)

 $D_4^{20} = 0.861$  (1)  $n_D^{20} = 1.4180$  (1)

1.4230 (3)

 $D_4^{10} = 0.8650$  (2)  $n_D^{16.5} = 1.4202$  (2)

[For prepn. of  $\bar{C}$  from 2,4-dimethylpentanol-2 (dimethyl-isobutyl-carbinol) [Beil. I-417, I<sub>1</sub>-(207), I<sub>2</sub>-(446)] by saturation with HCl (2) or as by-product during its reactn. with  $AlCl_3 + C_6H_6$  (3) see indic. refs.; for prepn. of  $\bar{C}$  from 2,4-dimethylpentanol-3 (di-isopropyl-carbinol) (1:6215) in 100% yield by saturation with HCl gas and stdg. 10 weeks at 20° (note rearrangement) (1).]

$\bar{C}$  with Mg in dry ether gives (1)  $RMgCl$ , which upon oxidation with  $O_2$  and subsequent hydrolysis gives 32% yield 2,4-dimethylpentanol-2 (dimethyl-isobutyl-carbinol), b.p. 130-131° at 733 mm.,  $D_4^{20} = 0.811$ ,  $n_D^{20} = 1.4166$  (1).

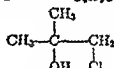
[For reactn. of  $\bar{C}$  with  $AlCl_3 + C_6H_6$  yielding 2,4-dimethyl-2-phenylpentane, b.p. 218°,  $D_4^{15} = 0.8741$ ,  $n_D^{16.5} = 1.49383$ , see (2).]

3: 7750 (1) Whitmore, Johnston, *J. Am. Chem. Soc.* 60, 2267 (1938). (2) Schreiner, *J. prakt. Chem.* (2) 82, 204 (1910). (3) Huston, Fox, Binder, *J. Org. Chem.* 3, 252-253 (1939).

## 3: 7752 1-CHLORO-2-METHYLPROPANOL-2

(Chloro-*ter*-butyl alcohol;  
chloro-trimethylcarbinol;  
isobutylene  $\alpha$ -chlorohydrin,  
 $\alpha,\alpha$ -dimethylethylene  $\alpha$ -chlorohydrin)

Beil. I - 382

I<sub>1</sub>-I<sub>2</sub>-(415)

B.P.

128-129° (1) (2)

127-129° (3)

127-128.5° (4)

126-128° (5) (6) (7)

126-127° at 736.4 mm. (8)

126.7° (9)

126.0-126.5° at 748.3 mm. (10)

71.0-71.5° at 100 mm. (10)

M.P.

-20° (5)  $D_4^{20} = 1.0628$  (9)

[See also 2-chloro-2-methylpropanol-1 (3:7905).]

Colorless liq somewhat sol. aq.; 100 g. aq. at 20° dis. 18.6 g.  $\bar{C}$  (note also that 100 g.  $\bar{C}$  at 20° dis. 19 g.  $H_2O$ ) (9). —  $\bar{C}$  forms with aq. a const.-boilg. mixt., h.p. 93-94° at 760 mm., contg. 34% aq (9).

[For prepn. of  $\bar{C}$  from 3-chloro-2-methylpropene-1 (methallyl chloride) (3:7145) or from 1-chloro-2-methylpropene-1 ( $\beta,\beta$ -dimethylvinyl chloride) (3:7120) by cat. hydration of their unsatd linkage (63-66% yield) see (9) (11); note that the former with 80%  $H_2SO_4$  at 0° or the latter with 90%  $H_2SO_4$  at -10° to 0° stirred for 2½ hrs., poured onto ice, and distilled gives 63-66% of the initial chloride as  $\bar{C}$ ; note that other acids can also be used for this hydration, e.g., 85%  $H_3PO_4$ , 70%  $HNO_3$ , 60%  $HClO_4$ , benzenesulfonic acid, etc., each having its own optimum conditions (9); note also that in this process some 32-18%

respectively of the initial chloride is not hydrated but partially isomerized to a mixt. contg. 90%  $\beta,\beta$ -dimethylvinyl chloride (3:7120) + 10% methallyl chloride (3:7145) irrespective of whichever one was initially employed (9).]

[For prepn. of  $\bar{C}$  from 1,2-dichloro-2-methylpropane (isobutylene dichloride) (3:7430) by liq.-phase hydrolysis of the more reactive halogen atom under neutral (or even slightly acidic or basic) conditions (best yield 48% by refluxing 18 hrs. with aq.) see (10).]

[For prepn. of  $\bar{C}$  from chloroacetone (3:5425) or ethyl chloroacetate (3:5700) with MeMgBr (yields: 60% (5), 38% (12)) (3) (6) or MeMgI (20% yield (4)) see (3) (5) (6) (12) (note that  $\bar{C}$  is accompanied (as a result of reaction of a second MeMgBr (13) (14)) by some 2-methylbutanol-2 (1:6160)); for prepn. of  $\bar{C}$  from isobutylene with HOCl (yields: 64% (6), 63% (1), 60% (7), 47% (2)) (5) (15), with  $Cl_2 + H_2O$  (16) (17) in pres. of 10%  $CuCl_2$  (80–85% yield (24)), or with *ter*-butyl-hypochlorite (3:7165) (18) see indic. refs.; for formn. of  $\bar{C}$  from 1,2-epoxy-2-methylpropane (isobutylene oxide) (1:6117) with HCl gas in ether see (19) (6) (4) (1) (note, however, that the prod. is a mixt. consisting of about  $\frac{2}{3}$   $\bar{C}$  contaminated with about  $\frac{1}{3}$  of the isomeric 2-chloro-2-methylpropanol-1 (3:7905)).]

[For formn. of  $\bar{C}$  from 1-amino-2-methylpropanol-2 hydrochloride with conc. HCl in s.t. at 100° see (12).]

[ $\bar{C}$  on reduction with Na/Hg in dil. HCl yields (2) (15) 2-methylpropanol-1 (isobutyl alcohol) (1:6165); this unexpected result presumably is due to intermediate formation of isobutylene oxide (1:6117) which on reduction opens the ring to give isobutyl alc. (not *ter*-butyl alcohol).]

[ $\bar{C}$  on protracted oxidation, e.g., with mixt. of 1.5 wt. pts. fuming  $HNO_3$  + 3.5 wt. pts. conc.  $HNO_3$  at 75° for 20 hrs. (2), gives traces of chloroacetone (3:5425) and a little oxalic acid (1:0445) and  $\alpha$ -chloroisobutyric acid (3:0235) (5).]

$\bar{C}$  on refluxing with aq. is slowly (e.g., 56% in 14 hrs. (2)) (21) converted to isobutyraldehyde (1:0120); note that this reaction carried out above 100° under press. (20) is greatly accelerated.

[ $\bar{C}$  with warm conc. HCl yields (10) (5) 1,2-dichloro-2-methylpropane (3:7430).]

$\bar{C}$  on solution in cold 45%  $H_2SO_4$  followed by warming loses  $H_2O$  and yields (9) a mixt. consisting of about 90% 1-chloro-2-methylpropene-2 (methallyl chloride (3:7145)) accompanied by about 10% 1-chloro-2-methylpropene-1 ( $\beta,\beta$ -dimethylvinyl chloride) (3:7120); a mixt. of these two chlorides has also been obt'd. by use of  $P_2O_5$  (1) (2) or anhydrous oxalic acid (2) (22).]

[ $\bar{C}$  added dropwise to dry powdered KOH, NaOH, CaO, or  $Ca(OH)_2$  loses HCl and gives (95% yield using NaOH (10), 67% using KOH (6)) 1,2-epoxy-2-methylpropane (isobutylene oxide) (1:6117), b.p. 56.0–56.5° cf. (24).]

[ $\bar{C}$  with aq. alkali ultimately yields 2-methylpropanediol-1,2 (isobutylene glycol) (1:6446) or its polymerization products; for study of kinetics of reaction of  $\bar{C}$  with aq. alk. see (4) (8).]

[ $\bar{C}$  with KCN in 4 vols. 80% alc. refluxed for 15–20 min. gives (45–50% yield (23))  $\beta$ -hydroxy-isovaleronitrile [Beil. III-328], b.p. 210–212° at 756 mm., 130–132° at 30 mm., f.p. -12°,  $D_4^{20} = 0.96762$ ,  $n_D^{20} = 1.42911$  (23).]

[ $\bar{C}$  with aq. 23%  $Et_3NH_2$  (4 moles) in s.t. at 100° for 8 hrs. gives (70–75% yield (25)) 1-(ethylamino)-2-methylpropanol-2, b.p. 156° ( $\bar{B}.HCl$ , m.p. 151° (25)). —  $\bar{C}$  with aq.  $Et_3NH$  refluxed 3–4 hrs. gives (60% yield (26)) 1-(diethylamino)-2-methylpropanol-2, b.p. 164–165° at 761 mm. (26),  $D_4^{20} = 0.8382$  (27),  $n_D^{20} = 1.4253$  (27) ( $\bar{B}.PhOH$ , m.p. 99–100° (26)). — For reactn. of  $\bar{C}$  with *N*-methylaniline, *N*-ethylaniline, or di-*n*-butylamine see (27).]

— Chloro-*ter*-butyl acetate: b.p. 154° at 760 mm. (28), 153–154° (5),  $D_4^{15} = 1.0626$  (28),  $n_D^{15} = 1.4340$  (28). [From  $\bar{C} + AcCl$  (5); also indirectly (28% yield (28)) from

isobutylene +  $N,N'$ -dichlorourea in  $\text{AcOH.}$ —[For analogous indirect prepn. of the formate, chloroacetate, and trichloroacetate see (28).]

— Chloro-*ter*-butyl benzoate: unreported.

— Chloro-*ter*-butyl *p*-nitrobenzoate: unreported.

— Chloro-*ter*-butyl 3,5-dinitrobenzoate: unreported.

① 1-(*N*-Phthalimido)-2-methylpropanol-2 (*N*-( $\alpha$ -hydroxyisobutyl)phthalimide): ndls. or lfts. from alc., m.p. 106–107° (12). [From  $\bar{\text{C}}$  + *K* phthalimide in s.t. at 150° for 4 hrs. (60% yield (12)).]

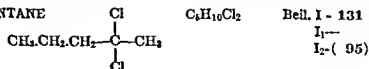
3:7752 (1) Michael, Leighton, *J. prakt. Chem.* (2) **64**, 103–104 (1901). (2) Michael, Leighton, *Ber.* **39**, 2157–2163 (1906). (3) Tiffeneau, *Compt. rend.* **134**, 775 (1902). (4) Nillson, Smith, *Z. physik. Chem.* A-**166**, 143–144 (1933). (5) Henry, *Rec. trav. chim.* **26**, 142–151 (1907); *Bull. acad. roy. Belg.* 1906, 523–557; *Cent.* 1906, II 1550–1551; *Compt. rend.* **142**, 131, 494–496 (1906). (6) Krassusky, *J. prakt. Chem.* (2) **75**, 241–247 (1007). (7) Krassusky, *J. Russ. Phys.-Chem. Soc.* **33**, 1–26 (1901); *Cent.* 1901, I 995–997. (8) Evans, *Z. physik. Chem.* **7**, 338–357 (1891). (9) Sparks, Nelson, *J. Am. Chem. Soc.* **63**, 384–388 (1941). (10) Sparks, Nelson, *J. Am.*

*U.S.* 2,042,222, May 26, 1936; *Cent.* 1937, I 3873; *N. V. de Bataafsche Petroleum Maatschappij*, French 791,644, 1, *Ber.* **54**, 3158–3160 (1921). (13) Henry, Tiffeneau, *Compt. rend.* **145**, 438 (1907). (15)

Butlerow, *Ann.* **114**, 25–26 (1867). (16) Kautter, *U.S.* 2,060,086, Oct. 17, 1936; *Cent.* 1937, I 3873; *N. V. de Bataafsche Petroleum Maatschappij*, French 799,805, June 20, 1936, *Cent.* 1936, II 3468; *C.A.* **30**, 8250 (1936). (17) Britton, Nutting, Huscher (to Dow Chem. Co.), *U.S.* 2,130,226, Sept. 13, 1938; *Cent.* 1939, I 1856; *C.A.* **32**, 9096 (1938). (18) *N. V. de Bataafsche Petroleum Maatschappij*, French 740,350, Jan. 24, 1933; *Cent.* 1933, I 2870. (19) Michael, Leighton, *Ber.* **39**, 2789–2795 (1906). (20) Groll, Kautter (to Shell Development Co.), *U.S.* 2,042,225, May 26, 1936; *Cent.* 1937, I 184; *C.A.* **30**, 4872 (1936); *Canadian* 363,685, Jan. 26, 1937; *Cent.* 1937, II 1661.

(21) Krassusky, *Bull. soc. chim.* (3) **24**, 236 (1900). (22) Krassusky, *J. prakt. Chem.* (2) **64**, 389–390 (1901). (23) Lemaire, *Rec. trav. chim.* **29**, 58–60 (1910); *Bull. acad. roy. Belg.* 1909, 83–159, *Cent.* 1909, I 1982. (24) Moureu, Dodé, *Bull. soc. chim.* (5) **4**, 286–289 (1937). (25) Krassusky, Kutenos, *Ukrain. Khim. Zhur.* **4**, Sci. Pt., 75–77 (1929); *Cent.* 1929, II 2174, *C.A.* **24**, 1083 (1930). (26) Krassusky, Stepanoff, *J. prakt. Chem.* (2) **115**, 321–324 (1927). (27) K. N. Campbell, B. K. Campbell, *Proc. Indiana Acad. Sci.* **49**, 101–104 (1939); *C.A.* **35**, 6460 (1941). (28) Likhoshervostov, Petrov, *J. Gen. Chem. (U.S.S.R.)* **9**, 2000–2008 (1939); *C.A.* **34**, 4381 (1940).

### 3:7755 2,2-DICHLOROPENTANE



B.P. 128–129° cor. (1)

44° at 31 mm. (1)

36–37° at 20 mm. (1)

$D_4^{20} = 1.040$  (1)  $n_D^{20} = 1.434$  (1)

The prod. upon which the above data are based was admittedly impure, still contg. 20% 2,3-dichloropentane (3:8010) q.v.

[For prepn. of  $\bar{\text{C}}$  from methyl *n*-propyl ketone (1:5415) with  $\text{PCl}_5$  see (1) (2) (3); for formn. of  $\bar{\text{C}}$  (together with other products) from pentane (1:8505) +  $\text{Cl}_2$  see (4).]

$\bar{\text{C}}$  with alc. KOH gives (2) 2-chloropentene-1 (3:7250) and pentyne-1 (1:8025). —  $\bar{\text{C}}$  on boilg. with  $\text{NaNH}_2$  in xylene gives (1) pentyne-1 (1:8025).

[For reactn. of  $\bar{\text{C}}$  with  $\text{SbF}_5$  yielding 2,2-difluoropentane, b.p. 59.8°,  $D_4^{20} = 0.8958$ ,  $n_D^{20} = 1.33570$ , see (3).]

3:7753 (1) Bourgeul, *Ann. chim.* (10) **3**, 220, 368–370 (1925); *Bull. soc. chim.* (4) **35**, 1634 (1921). (2) Bruylants, *Ber.* **8**, 411 (1875). (3) Henne, Renoll, Leicester, *J. Am. Chem. Soc.* **61**, 938–940

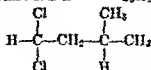


3:7880 (1) Hommelen, *Bull. soc. chim. Belg.* 42, 243-250 (1933). (2) Whitmore, Foster, *J. Am. Chem. Soc.* 64, 2966-2968 (1942). (3) Homeyer, Whitmore, Wallingford, *J. Am. Chem. Soc.* 65, 4211-4212 (1933). (4) Whitmore, Heyd, *J. Am. Chem. Soc.* 60, 2030-2031 (1938). (5) Whitmore, Popkin, Whitaker, Mattel, Zech, *J. Am. Chem. Soc.* 60, 2462-2464 (1938). (6) Whitmore, Whitaker, Mosher, Breivik, Wheeler, Miner, Sutherland, Wagner, Clapper, Lewis, Lux, Popkin, *J. Am. Chem. Soc.* 63, 643-654 (1941). (7) Whitmore, Homeyer (to Mallinckrodt, Chem. Works), U.S. 2,052,995, Sept. 1, 1939; *Cent.* 1936, II 3846; *C.A.* 30, 7125 (1936).

3:7885 *d,l*-4,4-DICHLORO-2-METHYLBUTANE

 $C_4H_{10}Cl_2$ 

Beil. I - 135


 $I_1-(47)$ 
 $I_2-$ 

B.P. 130° (1)

129.9-131.5° (2)

128-130° (3)

 $D_4^{25} = 1.05$  (1)

Colorless limpid liquid, insol. aq., sol. in alc. or ether.

[For prepn. of  $\bar{C}$  from isovaleraldehyde (1:0140) with  $PCl_5$  see (1) (2) (3); for formn. of  $\bar{C}$  by actn. of  $Cl_2$  (+ $I_2$ ) on diisocamyl sulfide see (4).]

$\bar{C}$  with KOH gives (1) (3) 4-chloro-2-methylbutene-3 (3:7215) and ultimately 3-methylbutyne-1 (isopropylacetylene) (1:8010), b.p. 28°.

$\bar{C}$  htd. with  $PbO$  +  $H_2O$  gives (4) isovaleraldehyde (1:0140).

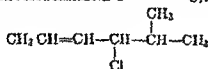
3:7885 (1) Ebersach, *Ann.* 100, 265-266 (1858) (2) Kohlrausch, *Monatsh.* 65, 197 (1935). (3) Bruylants, *Ber.* 8, 413-414 (1875). (4) Spring, Lecomte, *Bull. soc. chim.* (3) 48, 627 (1837).

3:7890 *d,l*-4-CHLORO-5-METHYLHEXENE-2

 $C_7H_{13}Cl$ 

Beil. I -

(*d,l*-3-Chloro-2-methylhexene-4)


 $I_1-$ 
 $I_2-(108)$ 

B.P. 130° (1)

38-40° at 8 mm. (2)

[For prepn. of  $\bar{C}$  from 2-methylhexen-4-ol-3 [Beil. I-447,  $I_2$ -(489)] with conc. HCl at ord. temp. (90% yield (2)) or with  $SOCl_2$  in pet. ether (1) see indic. refs.]

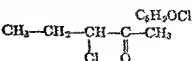
$\bar{C}$  with quinoline loses HCl on boilg. giving (1) 2-methylhexadiene-2,4 [Beil. I-257,  $I_2$ -(235)], b.p. 99° (1).]

$\bar{C}$  with diethylamine yields (3) 3-diethylamino-2-methylhexene-4, oil, b.p. abt. 175° (3).]

3:7890 (1) Staudinger, Muntwyler, Ruzicka, *Seibt. Helv. Chim. Acta* 7, 399 (1924). (2) Bottcher (to I.G.), *Ger.* 508,891, Oct. 2, 1930; *Cent.* 1930, II 3637; *C.A.* 25, 710 (1931). (3) Böttcher (to I.G.), *Ger.* 487,787, Dec. 16, 1929, *Cent.* 1930, I 1050.

3:7893 3-CHLOROPENTANONE-2

( $\alpha$ -Chloro-*n*-propyl methyl ketone)



Beil. I - 678

 $I_1-$ 
 $I_2-$ 

B.P. 130° (1)

130-133° (2)

63° at 95 mm. (3) cf. (7)

62-66° at 56 mm. (7)

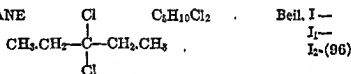
[For prepn. of  $\bar{C}$  from pentanone-2 (methyl *n*-propyl ketone) (1:5415) with  $Cl_2$  (yields: 35.5% (3), 85% crude (2)) cf. (6) or with  $SO_2Cl_2$  in  $C_6H_6$  (44% yield (7)) see indic. refs.; from ethyl  $\alpha$ -chloro- $\alpha$ -ethylacetacetate [Beil. III-694, III<sub>1</sub>-(241), III<sub>2</sub>-(438)] by ketonic cleavage with dil. HCl in s.t. at 180° for 4-6 hrs. see (1) cf. (7).]

[ $\bar{C}$  in abs. alc. treated with  $NH_3$  gas yields (2) 2,5-dimethyl-3,6-diethylpyrazine [Beil. XXIII-101], liq., b.p. 215-217°, forming with aq. a sublimable hydrate, m.p. 42.5°. (Note that 2-chloropentanone-3 (3:7935) similarly treated gives same prod.) —  $\bar{C}$  with equiv. amt. ethyl  $\beta$ -aminocrotonate [Beil. III-654, III<sub>1</sub>-(228), III<sub>2</sub>-(423)] in pres. of excess conc.  $NH_4OH$  gives (27.3% yield (4)) ethyl 2,5-dimethyl-4-ethylpyrrolecarboxylate-3 [Beil. XXII-33, XXII<sub>1</sub>-(501)], cryst. from dil. MeOH, m.p. 74-75° (4); note, however, m.p. 106-107° (5) reported for this prod. obtd. in a dif. way.]

[ $\bar{C}$  with thioformamide gives (29% yield (7)) 4-methyl-5-ethylthiazole, b.p. 169.5-170° at 745 mm., 78-79° at 25 mm. (7).]

3:7893 (1) Conrad, *Ann.* 186, 241-242 (1877). (2) D  metre-Vladesco, *Bull. soc. chim.* (3) 6, 832-834 (1891). (3) Korschun, *Bull. soc. chim.* (4) 3, 595-596 (1908). (4) Korschun, *Bull. soc. chim.* (4) 3, 594-595 (1908). (5) Vecchi, *Gazz. chim. ital.* 44, I 477 (1914). (6) Justoni, *Chimica e industria (Italy)* 24, 195-201 (1942); *Cent.* 1943, I 1659. (7) Buchman, Richardson, *J. Am. Chem. Soc.* 67, 397 (1945).

## 3:7895 3,3-DICHLOROP  NTANE



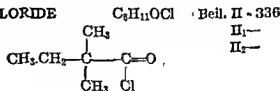
B.P. 131-132° at 760 mm. (1)  
32° at 14 mm. (1)

$D_4^{20} = 1.053$  (1)  $n_D^{20} = 1.442$  (1)

$\bar{C}$  has never been reported in completely pure form; the above material contains abt. 20% 2,3-dichloropentane (3:8010) q.v. (1).

[For prepn. of  $\bar{C}$  (together with other products) from diethyl ketone (1:5420) with  $PCl_5$  see (1).]

3:7895 (1) Bourge  l, *Compt. rend.* 178, 1559 (1924); *Bull. soc. chim.* (4) 35, 1635, (1924); *Ann. chim.* (10) 3, 371 (1925).

3:7900  $\alpha,\alpha$ -DIMETHYL-*n*-BUTYRYL CHLORIDE  
(Dimethyl-ethyl-acetyl chloride)

B.P. 132° at 760 mm. (6)  
131.8-132.4° at 748 mm. (1)  
131.7-131.9° (2)  
129.8° at 727 mm. (5)  
23° at 12 mm. (3)  
27° at 11 mm. (4)

$D_4^{20} = 0.9801$  (1)  $n_D^{20} = 1.4245$  (5)

$D_4^{20} = 0.9973$  (1)

[For prepn. of  $\bar{C}$  from 2,2-dimethylbutanoic acid-1 (1:1113) with  $SOCl_2$  (50% yield (5)) see (1) (5); with benzoyl chloride (yield not given) see (6).]

[For reactn. of  $\bar{C}$  with isobutyl zinc iodide yielding (3) 2,5,5-trimethylheptanone-4

(tetrahydroartemisaketone) see (3); for reactn. of  $\bar{C}$  with isopropyl MgBr yielding (by reducing actn.) 2,2-dimethylbutanol-1 (1:6204) and 2,4,4-trimethylhexanol-3 (5) see (5).]

$\bar{C}$  on hydrolysis yields 2,2-dimethylbutanoic acid-1 (1:1113) q.v. (for the amide, anilide, *p*-toluidide,  $\alpha$ -naphthalide, and other derivatives corresponding to  $\bar{C}$  see 1:1113).

3:7900 (1) Hommelen, *Bull. soc. chim. Belg.* 42, 243-250 (1933). (2) Kohlrausch, Pongratz, *Z. physik. Chem.* B-22, 383 (1933). (3) Ruzicka, Reichstein, Pulver, *Helv. Chim. Acta* 19, 618-649 (1936). (4) Reichstein, Rosenberg, Eberhardt, *Helv. Chim. Acta* 18, 723 (1935). (5) Whitmore, Foster, *J. Am. Chem. Soc.* 64, 2966-2968 (1942). (6) Degnan, Shoemaker, *J. Am. Chem. Soc.* 68, 104-105 (1946).

### 3:7003 CHLOROBENZENE (Phenyl chloride)

 $C_6H_5Cl$ 

Beil. V - 199

 $V_1$ -(109) $V_2$ -(148)

B.P.		F.P.	
132.10-132.12° cor.	(1)	-44.0° (21) (22)	$D_4^{25} = 1.1016$ (14)
132.07°	at 760 mm. (2)	-45.0° (23) (24)	1.1012 (31)
132.02°	at 761.8 mm. (3)	(7) (25)	1.1011 (32)
132.0°	at 760 mm. (4)	-45.1° (4)	1.10091 (4)
	(5) (6) (7) (8) (9) (10)	-45.2° (26) (27)	$n_D^{25} = 1.5222$ (14)
131.83°	at 760 mm. (11)	(28) (29)	1.5221 (28)
131.7°	at 760 mm. (12)	(8)	1.5217 (31)
131.6°	(13)	-45.29° (2)	1.5215 (36)
131.4-131.6°	at 748 mm. (14)	See Note 2.	$D_4^{20} = 1.1066$ (38)
130.7°	at 755 mm. (15)		1.10643 (33)
130.5°	at 755 mm. (16)		1.1064 (12)
129.6°	at 719 mm. (17)		1.10631 (4)
114.9°	at 468.5 mm. (17)		$n_D^{20} = 1.5251$ (37)
00.7°	at 292.8 mm. (17)		1.525 (2)
44.8°	at 30 mm. (18)		1.52479 (38)
See Note 1.			1.52459 (15)

 $D_4^{15} = 1.11172$  (4)

See Note 3.

 $n_D^{15} = 1.52748$  (4)

1.5272 (39)

See Note 4.

Note 1. For further data on b.p. of  $\bar{C}$  at various press. in range 98-758 mm. see (19), between 3-11, 188 mm., see (20)

Note 2. For details on m.p. of  $\bar{C}$  under high pressures see (26) (30).

Note 3. For details on  $D_4^1$  over range 0.3-123.6° see (34), over range -42.7° to +126° see (35).

Note 4. For details of change of refractive index with pressure see (40)

$\bar{C}$  is pract. insol. aq.; for precise data see (11) (225). —  $\bar{C}$  is very eas. sol. alc., ether,  $C_6H_6$ ,  $CHCl_3$ ,  $CS_2$ . — For detn. of  $\bar{C}$  in mixt. with  $C_6H_6$  and the dichlorobenzenes see (226) (227). — For use of  $\bar{C}$  as immersion fluid in refractometry see (228). — For toxicity of  $\bar{C}$  see (229). — For brief study of detn. of vapors of  $\bar{C}$  in air using a combustion method see (230).

Selected data and references on physical properties of mixts. of  $\bar{C}$  with other cpds (for additional data and references on many other systems see Beilstein).

Binary systems.  $\bar{C}$  with  $H_2O$  forms a const.-boilg. mixt., b.p. 90.2° at 760 mm., contg; 71.6%  $\bar{C}$  (41) (use in sepn. of  $\bar{C}$  from polychlorobenzenes see (69));  $\bar{C}$  with acetone (1:5400).



nitrobenzene, f.p./compn. data + diagram (eutectic, m.p.  $-50.7^{\circ}$  contg. 78.3 wt. %  $\bar{C}$ ) see (21);  $\bar{C}$  with pyridine, f.p./compn. data + diagram (eutectic, m.p.  $-63.5^{\circ}$ , contg. 54%  $\bar{C}$ ) and also  $n_D^{25}$ /compn. diag. see (28);  $\bar{C}$  with *o*-chlorotoluene (3:8245), f.p./compn. diagram (eutectic, m.p. abt.  $-71^{\circ}$ , contg. 39.4 mole %  $\bar{C}$ ) see (44);  $\bar{C}$  with *m*-dichlorobenzene (3:5960), f.p./compn. data, see (23);  $\bar{C}$  with benzoyl chloride (3:6240), f.p./compn. data see (45);  $\bar{C}$  + ethylene dibromide, f.p./compn. diag. (eutectic; m.p.  $-55^{\circ}$  contg. 83 mole %  $\bar{C}$ ) see (44); vapor-press. equil. see (46);  $\bar{C}$  + bromobenzene, f.p./compn. diagram (no eutectic) see (22) (24); for use in testing efficiency of distillation columns see (39);  $\bar{C}$  + iodobenzene, f.p./compn. diagram (eutectic, m.p.  $-51.5^{\circ}$ , contg. 57%  $\bar{C}$ ) see (22) (24);  $\bar{C}$  with fluorobenzene, f.p./compn. diagram (complex system) see (22) (24).

Ternary Systems.  $\bar{C}$  with aq. + HCl forms ternary const.-boilg. mixt., b.p.  $96.6^{\circ}$  at 756 mm., contg. 74.5 wt. %  $\bar{C}$  + 20.2 wt. % aq. + 5.3 wt. % HCl (41);  $\bar{C}$  with aq. + acetone, solubility diagram see (47);  $\bar{C}$  + ethylene glycol (1:6465) + acetone, soly. of system at  $23^{\circ}$  see (48).

Preparation of  $\bar{C}$ . Because of the magnitude of the literature on this topic only a few selected references can be given here; reference should also be made to Beil. V-199, VI-(109) and V<sub>2</sub>-(148).

[For prepn. of  $\bar{C}$  from  $C_6H_6$  with  $Cl_2$  in pres. of  $SnCl_4$  at  $30-40^{\circ}$  (49), with  $NOCl$  at  $425^{\circ}$  (50), with  $HCl$  +  $O_2$  (air) + cat. (51) see indic. refs.; for discussion of prepn. of industrial  $\bar{C}$  see (52); for study of photochem. chlorination of  $C_6H_6$  see (53).]

[For prepn. of  $\bar{C}$  from aniline via formn. of benzenediazonium chloride/ $ZnCl_2$  cpd. and btg. with molten phenol (40% yield  $\bar{C}$  + 26% hydroxybiphenyl + 20% diphenyl ether (54)) or by isolation of solid benzene diazonium chloride and cautious decompn. by warming in various org. solvents see (55); from *p*-chloroaniline via formn. of *p*-chlorobenzenediazonium chloride/ $ZnCl_2$  cpd. and btg. latter with EtOH (67% yield) or EtOH + Zn dust (60% yield) see (54); from phenylhydrazine by oxidn. with aq.  $FeCl_3$  at  $70^{\circ}$  (61% yield) or with  $HClO_3$  (30% yield) see (56); from  $C_6H_5SO_2Cl$  (60% yield (57)), sulfonyl chloride (57), (57)), other aromatic sulfonyl chlorides ( . . . . . amines (59), or *N*-chloro-*p*-chlorobenzaldimine (60), see indic. refs.]

[For formn. of  $\bar{C}$  from benzoyl chloride (3:6240) on htg. in porcelain tube at  $550-600^{\circ}$  see (61); from benzeneazotriphenylmethane on warming in  $CCl_4$  see (62); from bis-(*p*-chlorophenyl)zinc by reaction with aq. see (63); from phenylboric acid with  $Cl_2$ /aq. or refluxed with aq.  $CuCl_2$  (85% yield) see (64); from  $C_6H_6$  + *n*-butyl chlorosulfonate +  $AlCl_3$  (11% yield) see (65); from  $C_6H_6$  with  $SeCl_4$  +  $AlCl_3$  see (66); from 4-chlorodiphenyl sulfide by htg. with sulfur see (67); from 2-chlorobenzophenone (3:0715) or 4-chlorobenzophenone (3:1914) on fusion with  $KOH/NaOH$  see (68).]

Pyrolysis.  $\bar{C}$  passed over Pt wire at bright red heat (70) or through hot Fe tube (71) yields 4,4'-dichlorobiphenyl (3:4300) accompanied by biphenyl (1:7175), 4-chlorobiphenyl (3:1912), and other products.

Reduction.  $\bar{C}$  in EtOH at  $55^{\circ}$  with excess  $H_2$  at 3 atm. in pres. of Adams' cat. readily (72) yields cyclohexane (1:8405). —  $\bar{C}$  with  $H_2$  or  $NH_2.NH_2$  in MeOH or EtOH in pres. of  $Pd/CaCO_3$  gives (73) cf. (74) small yields of biphenyl (1:7175). —  $\bar{C}$  with Na in boilg. EtOH (75), or Na/Hg in EtOH (76), or Na in AmOH (77), or NaOAm in AmOH (78) is debrominated, but extent of reactn. varies with conditions. —  $\bar{C}$  with HI + P is unaffected at  $300^{\circ}$  but at  $375^{\circ}$  yields (79) benzene. —  $\bar{C}$  in aq. or dil. alc. alk. with  $H_2$  in pres. of Ni

splits off all (80) its halogen as HCl. —  $\bar{C}$  with  $H_2 + Ni$  at  $270^\circ$  yields (81) benzene + biphenyl.

Behavior with chlorine.  $\bar{C}$  with  $Cl_2$  may add or substitute or both according to conditions. —  $\bar{C}$  under dil. aq. NaOH with excess  $Cl_2$  in sunlight (82) or with  $Cl_2$  at  $0^\circ$  in dark as directed (83) (84) gives (90% yield (83)) heptachlorocyclohexane [Beil. V-23,  $V_2$ -(12)] (known in 2 stereoisomeric forms, " $\alpha$ ," m.p.  $146^\circ$  (82), " $\beta$ ," m.p.  $260^\circ$  (82)). [For study of relative amts. addition and substitution with  $\bar{C} + Cl_2$  see (85).]

$\bar{C}$  with  $Cl_2$  in pres. of  $AlCl_3$  (86),  $Al/Hg$  (87), or  $FeCl_3$  (88), or  $\bar{C}$  with  $SO_2Cl_2 + S_2Cl_2 + AlCl_3$  (89), or  $\bar{C}$  htd. with  $FeCl_3$  (89) or  $PbCl_2 \cdot 2NH_4Cl$  (90), gives mainly 1,4-dichlorobenzene (3:0980) accompanied by other products. —  $\bar{C}$  with  $Cl_2$  at  $400$ – $700^\circ$  in pres. of cat. yields (91) (92) 1,3-dichlorobenzene (3:5960) + 1,3,5-trichlorobenzene (3:1400) and other products.

Behavior with bromine.  $\bar{C}$  with  $Br_2$  (93) under aq (82) or in pres. of  $AlCl_3$  (94),  $Al/Hg$  (95),  $Al$  (99), or  $Fe$  (99), or  $\bar{C}$  htd. with  $FeBr_3$  (96), gives mainly 4-bromochlorobenzene [Beil. V-209,  $V_1$ -(116),  $V_2$ -(162)], m.p.  $66^\circ$ , together with other products; for study of rate in  $AcOH$  see (97). —  $\bar{C}$  with  $Br_2$  at elevated temp gives greatly increased proportion of meta-bromochlorobenzene; e.g.,  $\bar{C}$  with  $Br_2$  at  $475^\circ$  gives (98) 53% *m*-, 27% *p*-, and 20% *o*-bromochlorobenzenes.

Behavior with metals.  $\bar{C}$  with  $Li$  in dry ether under dry  $N_2$  gives (35–49% yield (100)) phenyllithium [Beil. XVI-1-(589)]; for reactns. of latter with fluoro, chloro, bromo, or iodobenzene see (101).

$\bar{C}$  on boilg. with  $Na$  yields (102)  $C_6H_6$ , biphenyl, and other products;  $\bar{C}$  with  $Na$  in boilg. toluene yields mainly (102)  $C_6H_6$  together with other prods. —  $\bar{C}$  with amylsodium (from amyl chloride +  $Na$ ) in lgr. gives (103) (104) (105) phenylsodium [Beil. XVI-1-(589)] which with  $CO_2$  gives (105) benzoic acid;  $\bar{C}$  with  $Na +$  diethyl carbonate in  $C_6H_6$  gives (79% yield (106)) (for use of other esters such as methyl benzoate, ethyl benzoate, or diethyl oxalate in ether see (107)) or  $\bar{C}$  with  $Na +$  benzophenone in  $C_6H_6$  gives (98% yield (106)) (108) triphenylcarbinol (1:5985). —  $\bar{C}$  with  $Na + AsCl_3$  in xylene gives (82% yield (109)) triphenylarsine,  $\bar{C}$  with  $Na + SbCl_3$  in xylene yields (109) triphenylstibine.

$\bar{C}$  with  $Mg/Cu$  alloy in pres. of  $I_2$  (110), or  $\bar{C}$  with  $Mg$  in s.t. at  $150$ – $160^\circ$  for 3 hrs. (111) (112), or  $\bar{C}$  refluxed with  $Mg + Cu_2Cl_2$  (113), gives (yields. 80% (110), 85% (111)) phenyl magnesium chloride.

Behavior with Al halides.  $\bar{C}$  does not react with  $AlCl_3$  even on long boilg. (dif. from bromobenzene and iodobenzene which react at once) (114). —  $\bar{C}$  with freshly prepared fused  $AlBr_3$  yields (115) bromobenzene.

Behavior with  $AlCl_3 +$  other compounds.  $\bar{C}$  (2 moles) with  $CCl_4$  (1 mole) +  $AlCl_3$  (1.75 moles) in  $CS_2$  gives (116) (117) bis-(4-chlorophenyl)dichloromethane [Beil. V-592], m.p.  $52$ – $53^\circ$ , together with other products;  $\bar{C}$  (6 moles) with  $CCl_4$  (1 mole) +  $AlCl_3$  (1 mole) htd. at  $60$ – $70^\circ$  gives mainly (118) 2-chlorophenyl-bis-(4-chlorophenyl)chloromethane [Beil. V-703], m.p.  $153^\circ$ , accompanied by a small amt. *trans*-(4-chlorophenyl)chloromethane [Beil. V-703], m.p.  $113^\circ$ .

$\bar{C}$  with  $AcCl$  (3:7065) or  $Ac_2O + AlCl_3$  yields *p*-chloroacetophenone (3:6735) q.v. for details.

$\bar{C} +$  furoic acid (1:0475) +  $AlCl_3$  gives (18% yield (119)) 6-chloronaphthoic acid-1 (3:4845);  $\bar{C} +$  methyl furoate (1:3452) +  $AlCl_3$  gives in good yield (120) methyl 6-chloro-1-naphthoate.

$\bar{C}$  with phthalic anhydride (1:0725) +  $AlCl_3$  gives (121) (122) (123) (124) *o*-(4-chlorobenzoyl)benzoic acid [Beil. X-750,  $X_1$ -(336)], m.p.  $147$ – $148^\circ$ , which on ring closure with

conc.  $\text{H}_2\text{SO}_4$  yields 2-chloroanthraquinone (3:4922) q.v. [For corresp. reactns. of  $\bar{\text{C}}$  with 4-bromophthalic anhydride (125), 4-sulfaphthalic anhydride (126), naphthalene-1,2-dicarboxylic acid anhydride (127), or naphthalene-2,3-dicarboxylic acid anhydride (128) see indic. refs.]

Miscellaneous condensations.  $\bar{\text{C}}$  with acetylene +  $\text{AlCl}_3$  gives (129) 1,2-bis(4-chlorophenyl)ethane (4,4'-dichlorodiphenyl) + other prods., cf. also (130). —  $\bar{\text{C}}$  with propylene in pres. of sulfonic acids at 86–130° gives (131) isopropylbenzene (cumene) (1:7440). —  $\bar{\text{C}}$  + hexene-3 +  $\text{H}_2\text{F}_2$  gives (25% yield (132)) 4-chloro-(1'-ethylbutyl)benzene. —  $\bar{\text{C}}$  + cyclohexene + conc.  $\text{H}_2\text{SO}_4$  gives (50% yield (133)) 4-chlorophenylcyclohexane. —  $\bar{\text{C}}$  + allyl chloride (3:7035) + conc.  $\text{H}_2\text{SO}_4$  gives (133) 1-chloro-2-(*p*-chlorophenyl)propane.

$\bar{\text{C}}$  + isopropyl alc. with 80%  $\text{H}_2\text{SO}_4$  at 70° gives (72% yield (134)) 4-chloro-isopropylbenzene (3:8705). —  $\bar{\text{C}}$  with *ter*-butyl alc. +  $\text{AlCl}_3$  gives (135) 4-chloro-*ter*-butylbenzene;  $\bar{\text{C}}$  with *ter*-amyl alc. +  $\text{AlCl}_3$  gives (135) 4-chloro-*ter*-amylbenzene.

$\bar{\text{C}}$  +  $\text{CO}$  +  $\text{AlCl}_3$  +  $\text{TiCl}_4$  at 60 atm. and 30–35° (136) or  $\bar{\text{C}}$  +  $\text{HCN}$  +  $\text{AlCl}_3$  at 100° for 6 hrs. (137) gives *p*-chlorobenzaldehyde (3:0765). —  $\bar{\text{C}}$  +  $\text{CO}$  + cat. + steam at 300–400° (138) (139) gives benzoic acid. —  $\bar{\text{C}}$  with paraformaldehyde +  $\text{ZnCl}_2$  (140) (142) or  $\bar{\text{C}}$  with formalin +  $\text{HCl}$  (141) or  $\bar{\text{C}}$  with chloromethyl methyl ether (3:7085) +  $\text{ZnCl}_2$  (142) or  $\bar{\text{C}}$  with bis-(chloromethyl) ether (3:5245) +  $\text{ZnCl}_2$  (142) yields *p*-chlorobenzyl chloride (3:0220) q.v. —  $\bar{\text{C}}$  with *p*-chlorobenzyl chloride (3:0220) +  $\text{H}_2\text{SO}_4$  yields (142) 4,4'-dichlorodiphenylmethane.

$\bar{\text{C}}$  with chloral (3:6210) or chloral hydrate (3:1270) + conc. or fuming  $\text{H}_2\text{SO}_4$  gives 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane ("DDT") (3:3298) q.v.

Hydrolysis.  $\bar{\text{C}}$  is unaffected by protracted boilg. with aq. or even alc. alk.; however, by use of increased temp. and press. especially in pres. of catalysts the hydrolysis of  $\bar{\text{C}}$  constitutes an extremely important industrial process for manufacture of phenol.

For general studies on the catalytic hydrolysis of  $\bar{\text{C}}$  to phenol with steam at elevated temperatures see (143) (144) (145) (146); for patents employing this method see (147)–(159) incl. — For résumé of prepn. of phenol via Raschig method ( $\text{C}_6\text{H}_6$  +  $\text{HCl}$  +  $\text{O}_2$  to  $\bar{\text{C}}$  with subsequent hydrolysis) see (160); for relevant patents see (161) (162) (163). — For sepn. of products of hydrolysis see (41) (164).

$\bar{\text{C}}$  may also be hydrolyzed to phenol by means of aq.  $\text{NaOH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , etc., at elevated temp. and press. especially in pres. of catalysts, notably copper: for impt. general review of these methods up to 1927 see (165); for general discussion see (166); for recent patents on this process and its variants see (167)–(182) incl. — For conv. of  $\bar{\text{C}}$  with alk. to 4-hydroxybiphenyl (1:1585) see (183) or to diphenyl ether (1:7125) see (184) (185) (186).

$\bar{\text{C}}$  htd. with aq.  $\text{Na}_2\text{S}$ ,  $\text{NaSH}$ , or  $\text{H}_2\text{S}$  under press. gives (187) (188) (189) (190) diphenyl sulfide and/or thiophenol. —  $\bar{\text{C}}$  +  $\text{H}_2\text{S}$  + cat. at 700° gives (191) thiophenol.

[For use of  $\bar{\text{C}}$  in prepn. of sulfur dyes by htg. with sulfur see (192) (193).]

Ammonolysis.  $\bar{\text{C}}$  with dry  $\text{NH}_3$  does not react even in pres. of  $\text{Cu}$  +  $\text{I}_2$  and high temp. and press. (194). — However,  $\bar{\text{C}}$  with conc. aq.  $\text{NH}_4\text{OH}$  htd. at high temp. and press. especially in pres. of  $\text{Cu}$ ,  $\text{Cu}$  cpds., or other cat. yields aniline and/or diphenylamine; for general discussion of this reactn. see (195) (196) (197) (198) (199); for illustrative patents see (200)–(208) incl.; for purification of reactn. prod. see (209) (210). — For behavior of  $\bar{\text{C}}$  with  $\text{Na}$  in liq.  $\text{NH}_3$  (211) and its use in detn. of halogen content of  $\bar{\text{C}}$  (212) see indic. refs. — For behavior of  $\bar{\text{C}}$  with  $\text{KNH}_2$  in liq.  $\text{NH}_3$  see (213) (214).

Nitration.  $\bar{\text{C}}$  on mononitration, e.g., with mixt. of 10 ml.  $\text{HNO}_3$  ( $D = 1.52$ ) + 50 ml.  $\text{HNO}_2$  ( $D = 1.48$ ) for 25 g.  $\bar{\text{C}}$  at 0° (215), gives a prod. contg. 69.9% *p*-chloronitrobenzene [Beil. V-243,  $V_1$ -(130),  $V_2$ -(183)], m.p. 82°, together with 29.8% *o*-chloronitrobenzene [Beil. V-241,  $V_1$ -(129),  $V_2$ -(180)], m.p. 32°; the *p/o* ratio is but little different at –30°;

3:0590 *p*-CHLOROPHENYLACETYLENE $C_8H_7Cl$ 

Beil. S.N. 474



M.P. 45.4-46.1° (1)

43.5-44° (2)

[For prepn. of  $\bar{C}$  from *p*-chloro- $\alpha$ -chlorostyrene by elimination of HCl with 25% alc. KOH (36% yield (1)) (2) see indic. refs.]

[For study of dipole moment see (3).]

[ $\bar{C}$  with  $I_2$  in liq.  $NH_3$  at  $-34^\circ$  readily gives (98% yield (1)) *p*-chlorophenyl-iodo-acetylene, m.p. 84.7-85.0° (1).]

[ $\bar{C}$  with  $NH_3/Cu_2Cl_2$  as directed gives (50% yield (5)) di-(*p*-chlorophenyl)biacetylene, m.p. 258° (5).]

④ Di-(*p*-chlorophenylethynyl)mercury: m.p. 221-222° (2), 221.5° (1). [From  $\bar{C}$  in alc. with alk.  $K_2HgI_4$  according to (4); note that m.p. of this prod. is only slightly higher than that (213-214°) for the corresp. prod. from *o*-chlorophenylacetylene (3:9497).]

3:0590 (1) Vaughn, Nieuwland, *J. Am. Chem. Soc.* 56, 1307-1309 (1934). (2) Otto, *J. Am. Chem. Soc.* 56, 1393-1394 (1934). (3) Otto, Wenzke, *J. Am. Chem. Soc.* 56, 1314-1315 (1934). (4) Johnson, McEwen, *J. Am. Chem. Soc.* 48, 471 (1926). (5) Zalkind, Fundyler, *J. Gen. Chem. (U.S.S.R.)* 9, 1725-1728 (1939); *C.A.* 34, 3719 (1940).

## 3:0610 2,3,5-TRICHLOROTOLUENE

 $C_7H_3Cl_3$ 

Beil. V - 299


 $V_1-$   
 $V_2-$ 

M.P. 45-46° (1) B.P. 220-231° at 757 mm. (1)

[For prepn. of  $\bar{C}$  from 3,5-dichloro-2-aminotoluene [Beil. XII-837] or from 2,5-dichloro-3-aminotoluene [Beil. XII-872] via diazotization and use of  $CuCl_2$  reactn. see (1); for formn. of  $\bar{C}$  from 3,5-dichlorotoluene (3:6310) with  $Cl_2$  in pres. of  $Al/Hg$  see (2).]

[ $\bar{C}$  with  $Cl_2$  in pres. of  $Al/Hg$  yields (3) 2,3,5,6-tetrachlorotoluene (3.2575).]

$\bar{C}$  on mononitration with cold fuming  $HNO_3$  (1) yields 2,3,5-trichloro-4(or 6)-nitrotoluene [Beil. V-333], ndls. from alc. or  $AcOH$ , m.p. 58-59° (1);  $\bar{C}$  on dinitration with 6 pts. fuming  $HNO_3$  + 4 pts. conc.  $H_2SO_4$  yields 2,3,5-trichloro-4,6-dinitrotoluene [Beil. V-345], ndls. from alc. +  $AcOH$ , m.p. 149-150° (1).

$\bar{C}$  on oxidn. with dil.  $HNO_3$  in a s.t. at  $140^\circ$  yields (1) 2,3,5-trichlorobenzoic acid (3:4485), m.p. 162° (1).

3:0610 (1) Cohen, Dakin, *J. Chem. Soc.* 81, 1329-1331 (1902). (2) Cohen, Dakin, *J. Chem. Soc.* 81, 1343-1344 (1902). (3) Cohen, Dakin, *J. Chem. Soc.* 85, 1284 (1904).

## 3:0618 2,4,6-TRICHLORO-3-METHYLPHENOL

 $C_7H_5OCl_3$ 

Beil. VI —

(2,4,6-Trichloro-*m*-cresol) $VI_1-$  (189) $VI_2-$  (356)

M.P. 46° (1) (2) B.P. 265°

45° (3)

102-163° nt 28 mm. (3)

[For prepn. of  $\bar{C}$  from *m*-cresol (1:1730) in aq. alk. with excess  $Cl_2$  (3) or from *m*-cresol with  $Cl_2$  in the dark (2) see indic. refs. (note that *m*-cresol with  $Cl_2$  in sunlight yields (2)

3:7917	<i>d,l</i> -2-CHLOROPROPANOL-1 (Propylene $\beta$ -chlorohydrin; $\beta$ -chloro- <i>n</i> -propyl alcohol)	$\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\underset{\text{OH}}{\text{CH}_2}$	$\text{C}_3\text{H}_7\text{OCl}$	Beil. I - 356 I <sub>1</sub> -(180) I <sub>2</sub> -(369)
B.P. 133-134°	cor. at 762 mm. (1)	$D_{20}^{20} = 1.103$	(1)	$n_D^{20} = 1.43023$ (1)
133-134°	at 761 mm. (2)			
133-134°	at 760 mm. (3)	$D_{15}^{15} = 1.4505$	(9)	$n_D^{15} = 1.4766$ (9)
133°	(10)			
94°	at 8 mm. (9)			

[See also 1-chloropropanol-2 (3:7747).]

[For prepn. of  $\bar{\text{C}}$  from its acetate (see below) by alcoholysis with excess boilg. dry MeOH for 8 hrs. (83% yield) see (1); note that this prepn. really starts from the isomeric 1-chloropropanol-2, the conversion of which to  $\bar{\text{C}}$  involves the following steps: reaction with KOAc yielding  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2(\text{OAc})$ , conversion of latter with  $\text{HCl} + \text{ZnCl}_2$  to  $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2(\text{OAc})$ , and finally alcoholysis to  $\bar{\text{C}}$  as mentioned above (1) (4); for formn. of  $\bar{\text{C}}$  by alk. hydroly. of its trichloroacetate see (9) ]

[Note that although  $\bar{\text{C}}$  is formed in other ways (e.g., from propanediol-1,2 (propylene glycol) (1:6455) with  $\text{HCl}$  or  $\text{S}_2\text{Cl}_2$  (5), from 2,3-epoxybutane (propylene oxide) (1:6115) by addn. of  $\text{HCl}$  (5), from propylene with  $\text{HOCl}$  (5), or from  $\alpha$ -chloro-*n*-propylamine with  $\text{HNO}_2$  (6)) the product of these reactions appears to be (5) (6) an inseparable mixt. of about 40%  $\bar{\text{C}}$  with 60% of the isomeric 1-chloropropanol-2 (3:7747).]

Reactions of the halogen atom of  $\bar{\text{C}}$ . [ $\bar{\text{C}}$  when added dropwise to conc. aq. KOH loses  $\text{HCl}$  yielding (1) 2,3-epoxybutane (propylene oxide) (1:6115), b.p. 35°. —  $\bar{\text{C}}$  with KCN in 80% alc. contg. some NaI gives on warming (60% yield (2))  $\beta$ -hydroxy-*n*-butyronitrile [Beil. III-309, III<sub>2</sub>-(221)], b.p. 214-215° (2); note that this is not the product to be expected from simple replacement of Cl by CN and apparently results from preliminary formation of propylene oxide to which HCN then adds so as to give a straight (rather than forked) carbon chain.]

Reactions of the OH group of  $\bar{\text{C}}$ . [ $\bar{\text{C}}$  reacts normally as a substituted primary alc. giving ethers, esters, oxidn. products, etc.]

[ $\bar{\text{C}}$  readily gives the corresp. ethers; e.g.,  $\bar{\text{C}}$  with  $\text{Me}_2\text{SO}_4$  on warming gives (7)  $\beta$ -chloro-*n*-propyl methyl ether, b.p. 98-99° at 756 mm.,  $D_{15}^{20} = 0.9946$ ,  $n_D^{20} = 1.40754$  (7);  $\bar{\text{C}}$  with  $\text{EtOH} + \text{conc. H}_2\text{SO}_4$  on htg. gives (54% yield (7))  $\beta$ -chloro-*n*-propyl ethyl ether, b.p. 116-117° at 758 mm.,  $D_{15}^{20} = 0.9828$ ,  $n_D^{20} = 1.41285$  (7); for corresp. formn. of ethers with *n*-propyl alc. (1:6150) and with allyl alc. (1:6145) see (7).]

[ $\bar{\text{C}}$  (1 mole) with  $\text{SO}_2\text{Cl}_2$  (2.5 moles) at 130° gives (16% yield (7)) bis-( $\beta$ -chloro-*n*-propyl) ether, b.p. 188° at 762 mm.,  $D_{15}^{20} = 1.109$ ,  $n_D^{20} = 1.4467$  (7); note that this ether is not obtd. from  $\bar{\text{C}}$  with conc.  $\text{H}_2\text{SO}_4$  (7).]

[ $\bar{\text{C}}$  on oxidn. with 3 wt. pts. conc.  $\text{HNO}_3$  as directed (8) (2) gives (85% yield (2))  $\alpha$ -chloropropionic acid (3:6125), accompanied by some acetic acid (1:1010) and oxalic acid (1:0445); note that  $\bar{\text{C}}$  on oxidn. with chromic acid yields no  $\alpha$ -chloropropionic acid but only acetic acid (1:1010) and formic acid (1:1005) (2).]

—  $\beta$ -Chloro-*n*-propyl acetate [Beil. II-129, II<sub>1</sub>-(58), II<sub>2</sub>-(139)]: oil, insol. aq., b.p. 151-152° at 768 mm. (11), 152-153° at 750 mm. (1). [Prepd. indirectly; furthermore the prods. reported may be contaminated with some of the isomeric  $\beta$ -chloroisopropyl acetate cf. (10).]

—  $\beta$ -Chloro-*n*-propyl benzoate: unreported.

—  $\beta$ -Chloro-*n*-propyl *p*-nitrobenzoate: unreported.

—  $\beta$ -Chloro-*n*-propyl 3,5-dinitrobenzoate: unreported.

for f.p./compa curve of system *p*-chloronitrobenzene/*o*-chloronitrobenzene (eutectic, m.p. 14.7°, contg. 33.1% *p*-isomer) see (215). — For mononitration using 0.9 g. of 70%  $\text{HNO}_3$  + 1.29 g. 94%  $\text{H}_2\text{SO}_4$  per gram of  $\bar{\text{C}}$  (216) or using nitrosulfonic acid (from fung.  $\text{HNO}_3$  treated with  $\text{SO}_2$ ) at 30° (217) or using  $\text{Fe}(\text{NO}_3)_3$  in  $\text{Ac}_2\text{O}$  at 40–45° (218) see indic. refs. — Note that no appreciable amt. of *m*-chloronitrobenzene is formed by direct nitration of  $\bar{\text{C}}$ .

$\bar{\text{C}}$  on dinitration, e.g., with 5 wt. pts. of a mixt. consisting of equal wts. of 92.8%  $\text{HNO}_3$ , 93.3%  $\text{H}_2\text{SO}_4$ , and fung.  $\text{H}_2\text{SO}_4$  (contg. 14.2%  $\text{SO}_3$ ) at 95° for 2 hrs. (219) gives 96.7% yield 2,4-dinitrochlorobenzene [Beil. V-263, V-(137),  $\text{V}_2$ -(196)], cryst. from alc., m.p. 52–53°. [The other dinitro isomers are known but need not be discussed here.]

Sulfonation.  $\bar{\text{O}}$  is insol. in cold conc.  $\text{H}_2\text{SO}_4$ ; however,  $\bar{\text{C}}$  on warming or on stdg. at room temp. for 48 hrs. (220) with equal wt. conc.  $\text{H}_2\text{SO}_4$  dissolves and later ppts. *p*-chlorobenzenesulfonic acid [Beil. XI-54, XI-(14)], anhydrous cryst. from  $\text{CHCl}_3$ , m.p. 92–93° (220), monohydrate from aq., m.p. 67° (221). —  $\bar{\text{C}}$  with fung.  $\text{H}_2\text{SO}_4$  (10%  $\text{SO}_3$ ) below 60° for 1 hr. then poured into 6 vols. satd. aq.  $\text{NaCl}$  soln. gives (222) (223) sodium salt of *p*-chlorobenzenesulfonic acid which with  $\text{PCl}_5$  yields corresp. sulfonyl chloride (see below). — For reactn. of  $\bar{\text{C}}$  with  $\text{ClSO}_3\text{H}$  see below. — [The corresp. bis-(4-chlorophenyl) sulfone [Beil. VI-327, VI-(149)] which may be formed in small amt. has m.p. 147–148°.] [For study of kinetics of sulfonation of  $\bar{\text{C}}$  see (231).]

① *p*-Bromochlorobenzene:  $\bar{\text{C}}$  with 0.25–0.50 mole  $\text{Br}_2$  at 60° in pres. of  $\text{Fe}$  gives (88% yield (99)) *p*-bromochlorobenzene, cryst. from alc., m.p. 67–68°.

② 2,4-Dinitrochlorobenzene:  $\bar{\text{C}}$  on htg. with mixt. of  $\text{HNO}_3$  +  $\text{H}_2\text{SO}_4$  (see above under nitration) at 95° for 2 hrs. gives (96.7% yield (219)) 2,4-dinitrochlorobenzene, cryst. from alc., m.p. 52–53°.

③ 4-Chlorobenzenesulfonamide:  $\bar{\text{C}}$  with  $\text{ClSO}_3\text{H}$  in  $\text{CHCl}_3$  as directed (224) gives 4-chlorobenzenesulfonyl chloride, cryst. from dry ether, m.p. 53°, which by boilg. with conc.  $\text{NH}_4\text{OH}$  or htg. with solid  $(\text{NH}_4)_2\text{CO}_3$  for 30 min. at 100° gives 4-chlorobenzenesulfonamide, cryst. from dil. alc., m.p. 142–143° u.c. (224).

3:7903 (1) Brooks, Hobbs, *J. Am. Chem. Soc.* 62, 2851 (1940). (2) Stull, *J. Am. Chem. Soc.* 59, 2729 (1937). (3) Feitler, *Z. physik. Chem.* 4, 63 (1889). (4) Timmermans, Martin, *J. chim. phys.* 23, 780–782 (1926). (5) Lecat, *Rec. trav. chim.* 46, 242 (1927). (6) Grimm, Patrick, *J. Am. Chem. Soc.* 45, 2799 (1923). (7) Timmermans, van der Horst, Onnes, Co Young, *Proc. Roy. Dublin Soc.* 12, 424 (1910). (8) 244–269 (1909), *Cent.* 1910, II 442. (9) Belg. 24,

(11) Gross, Saylor, *J. Am. Chem. Soc.* 53, 1748 (1931). (12) Matthews, *J. Am. Chem. Soc.* 61, 619 (1939). (13) Thomson, *J. Chem. Soc.* 3, 56 (1935). (14) Hurd, Smyth, *J. Am. Chem. Soc.* 61, 362–363 (1939). (15) Ramsay, Young, *Z. physik. Chem.* 1, 1 (1889).

(21) Hrynakowski, Szmyt, *Z. physik. Chem.* A-183, 110–112 (1938). (22) Pascal, *Bull. soc. chim.* (4) 13, 745–752 (1913). (23) Timmermans, *Bull. soc. chim. Belg.* 43, 633 (1934). (24) L. Klemm, W. Klemm, G. Schiemann, *Z. physik. Chem.* A-163, 384–386 (1933). (25) Timmermans, *Bull. soc. chim. Belg.* 25, 300–327 (1911); *Cent.* 1911, II 1015. (26) Bridgman, *J. Chem. Phys.* 9, 794–795 (1941). (27) Skau, *J. Phys. Chem.* 37, 612–613 (1933). (28) Burnham, Madgen, *J. Chem. Soc.* 1936, 790–792. (29) Menshutkin, *J. Russ. Phys.-Chem. Soc.* 43, 402 (1911).

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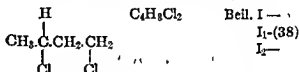
from dextrorotatory amyl chloride by photochemical chlorination with  $\text{SO}_2\text{Cl}_2$  in pres. of benzoyl peroxide see (4).]

$\bar{\text{C}}$  on boilg. with aq.  $\text{K}_2\text{CO}_3$  gives (1) (together with other products) 1-chloro-2-methylbutene-1 (3:7303), b p. 96-97°.

$\bar{\text{C}}$  on oxidn. with  $\text{KMnO}_4$  gives (2) butanone-2 (ethyl methyl ketone) (1:5405).

3:7920 (1) Chalmers, *Trans. Roy. Soc. Can.* (3) 22, III 69-78 (1928). (2) Gutner, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1062-1067 (1938); *Cent.* 1939, II 4221; *C.A.* 33, 3755 (1939). (3) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, II 4222; *C.A.* 33, 4190 (1939). (4) Brown, Kharasch, Chao, *J. Am. Chem. Soc.* 62, 3437-3439 (1940).

### 3:7925 1,3-DICHLOROBUTANE



B.P. 134° (1)

$D_4^{20} = 1.1158$  (3)

$n_D^{20} = 1.445$

131-133° at 758 mm. (3)

[For prepn. from butanediol-1,3 by btg. in s.t. with conc.  $\text{HCl}$  (satd. at 0°) see (1); for prepn. from 1-chlorobutane (*n*-butyl chloride) (3:7160) by actn. of  $\text{Cl}_2$  in light (other products also being formed) see (2) (3) (4) (5); for prepn. from 2-chlorobutane (3:7125) by actn. of  $\text{Cl}_2$  see (6).]

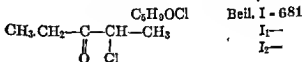
$\bar{\text{C}}$  on passing over alkali ( $\text{NaOH}$ ,  $\text{K}_2\text{CO}_3$ , soda-lime, etc.) at elevated temperatures (e.g., 700-750°) yields butadiene-1,3. [For studies of this reaction see (2) (4) (5).]

$\bar{\text{C}}$  is readily saponified with aq.  $\text{K}_2\text{CO}_3$  to butanediol-1,3 (1:6482) (6).

3:7926 (1) Fargher, Perkin, *J. Chem. Soc.* 105, 1356 (1914). (2) Muskat, Northrup, *J. Am. Chem. Soc.* 52, 4050-4052 (1930). (3) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 7, 893-896 (1937); *Cent.* 1938, II 2575; *C.A.* 31, 5755 (1937). (4) Carothers (to du Pont), U.S. 2,038,593, U.S. 2,070, Churbakov,

### 3:7935 2-CHLOROPENTANONE-3

( $\alpha$ -Chloroethyl ethyl ketone;  
 $\alpha$ -chlorodiethyl ketone)



B.P. 135° (1) (2)

145° (3)

Oil, insol. aq., sol. alc., ether.

[For prepn. of  $\bar{\text{C}}$  from pentanone-3 (diethyl ketone) (1:5420) with  $\text{Cl}_2$  (3) (4), with  $\text{Cl}_2$  in pres. of aq. +  $\text{CaCO}_3$  (86% yield (1)), or with  $\text{Cl}_2$  in vapor-phase chlorination (4) see indic. refs.; from 4-chloro-4-methyl-3-ethylisoxazolone-5 [Beil. XXVII-163] with hydrochloric acid see (2).]

$\bar{\text{C}}$  on reduction with  $\text{H}_2$  yields (3) pentanone-3 (1:5420).

$\bar{\text{C}}$  does not (3) form a cpd. with satd. aq.  $\text{NaHSO}_3$  soln.

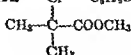
$\bar{\text{C}}$  dis. readily in aq. alk. yielding a soln. (presumably contg. pentanone-3-ol-2) which readily reduces  $\text{NH}_4\text{OH}/\text{AgNO}_3$  and reduces Fehling's soln. on warming (3).

[ $\bar{\text{C}}$  in abs. alc. treated with  $\text{NH}_3$  gas yields (3) 2,5-dimethyl-3,6-diethylpyrazine [Beil. XXIII-101], liq., b.p. 215-217°, forming with aq. a sublimable hydrate, m.p. 42.5°. (Note that 3-chloropentanone-2 (3:7893) similarly treated gives the same prod.)]

— 2-(Phthalimido)propanol-1 (*N*-( $\beta$ -hydroxyisopropyl)phthalimide): lfts. from EtOAc m.p. 99–101° (10). [Prepd. indirectly (10); note that the prod. obtd. (10) from  $\bar{C}$  with K phthalimide in a.t. at 200–230° was the isomeric 1-(phthalimido)propanol-2, m.p. 88–89° (10), but whether this result was due to contamination of  $\bar{C}$  with the isomeric 1-chloro-propanol-2 (3:7747) or the rearr. has never been clarified.]

3:7917 (1) Henry, *Rec. trav. chim.* 22, 327–333 (1903). (2) Dewael, *Rec. trav. chim.* 33, 504–507 (1924). (3) Henry, *Rec. trav. chim.* 22, 209–210 (1903). (4) Henry, *Bull. acad. roy. Belg.* 1902, 445–494; *Cent.* 1902, II 929. (5) Smith, *Z. physik. Chem.* 93, 59–85 (1919). (6) Smith, *Platon, Ber.* 55, 3150–3155 (1922). (7) Dewael, *Bull. soc. chim. Belg.* 34, 343–346 (1925). (8) Henry, *Rec. trav. chim.* 22, 341–344 (1903). (9) Gayler, Waddle, *J. Am. Chem. Soc.* 63, 3359 (1941). (10) Gabriel, Ohle, *Ber.* 50, 807, 812 (1917).  
(11) Dewael, *Bull. soc. chim. Belg.* 39, 400 (1930).

3:7918 METHYL  $\alpha$ -CHLOROISOBUTYRATE  $\text{C}_5\text{H}_9\text{O}_2\text{Cl}$  Beil. S.N. 162



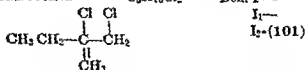
B.P. 135°	at 760 mm. (7)	$D_{15}^{25} = 1.0893$ (3)	$n_D^{25} = 1.4122$ (7)
133–135°	at 760 mm. (1) (2)		
128–129.5°	at 763 mm. (3)		$n_D^{15} = 1.4019$ (3)
64–65°	at 55 mm. (3)		
42–44°	at 17 mm. (7)		

[For prepn. of  $\bar{C}$  from  $\alpha$ -chloroisobutyric acid (3:0235) with MeOH see (3) (4); for formn. of  $\bar{C}$  as by-product of reactn. of methyl  $\alpha$ -hydroxyisobutyrate (1:3206) with phosgene (3:5000) + pyridine see (1) (2) (6).]

[ $\bar{C}$  on htg. at 500–510° (1), or passed over silica gel at 300° (4), or htd. with anhydrous  $\text{FeCl}_3$  for 4 hrs. at 100° (5), or htd. with quinoline in pres. of hydroquinone (3), gives (83% yield (5)) methyl methacrylate, b.p. 100–101°.]

3:7918 (1) Burns, Jones, Ritchie, *J. Chem. Soc.* 1935, 717. (2) Ritchie, *J. Chem. Soc.* 1935, 1059. (3) Zal'kind, Markov, *J. Applied Chem. (U.S.S.R)* 10, 1042–1044 (1937), *Cent.* 1938, II 2421; *C.A.* 32, 1652 (1938). (4) du Pont Co. & Loder, *Brit.* 428,223, June 6, 1935, *Cent.* 1936, I 179; *C.A.* 29, 6607 (1935). (5) Barrett (to du Pont Co.), U.S. 2,013,648, Sept. 10, 1935; *Cent.* 1936, I 3217, *C.A.* 29, 6902 (1935). (6) Imperial Chem. Ind. & Ritchie, Jones, Burns, *Brit.* 424,885, March 4, 1935, *Cent.* 1936, I 2440, *C.A.* 29, 5124 (1935). (7) Kahovec, Kohlrausch, *Monatsh.* 74, 116 (1943).

3:7920 *d,l*-1,2-DICHLORO-2-METHYLBUTANE  $\text{C}_4\text{H}_{10}\text{Cl}_2$  Beil. I —

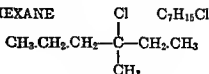


B.P. 133–135°	(1)	$D_4^{20} = 1.0785$ (1)	$n_D^{25} = 1.4432$ (4)
133.5° at 760 mm. (calcd.)	(4)	1.0766 (4)	
71.5° at 100 mm.	(4)		

[For prepn. of  $\bar{C}$  from 1,2-epoxy-2-methylbutane (1) with  $\text{PCl}_5$  see (1); for formn. of  $\bar{C}$  (together with other products) from 2-methylbutene-1 (unsym.-ethyl-methyl-ethylene) (1:8210) with  $\text{Cl}_2$  at  $\sim 5$  to  $\sim 17^\circ$  see (2) (3), for formn. of  $\bar{C}$  (together with other products)



## 3:7950 3-CHLORO-3-METHYLHEXANE

(Ethyl-methyl-*n*-propyl-carbinyl chloride) $\text{C}_7\text{H}_{15}\text{Cl}$ 

Beil. I —

I<sub>1</sub>-(58)I<sub>2</sub>-(119)

B.P. abt. 135°	(1)	$D_4^{20} = 0.8787$	(4)	$n_D^{20} = 1.4250$	(2)
62-63°	at 62 mm. (2)			1.4283	(3)
41°	at 20 mm. (3)			$n_D^{18} = 1.4280$	(5)
39-40°	at 16 mm. (4)			1.4275	(5)
32.0-32.5°	at 12 mm. (5)	$D_4^{14} = 0.875$	(5)	$n_D^{15} = 1.42705$	(4)
		0.872	(5)		

[For prepn. of  $\bar{C}$  from 3-methylhexanol-3 (ethyl-methyl-*n*-propyl-carbinol) {Beil. I-416, I<sub>1</sub>-(206), I<sub>2</sub>-(445)} (2) with dry HCl at 10-15° (90% yield (2)) or with HCl (4) see (2) (4); for formn. of  $\bar{C}$  as a by-product of the reactn. of the above carbinol with  $\text{C}_6\text{H}_6 + \text{AlCl}_3$  (main prod. 45% yield of 3-methyl-3-phenylhexane, b.p. 106-107° at 20 mm.,  $n_D^{20} = 1.4964$ ) see (3); for formn. of  $\bar{C}$  from 3-methylhexene-2 (1:8322) with conc. HCl see (5); for formn. of  $\bar{C}$  from ethyl-methyl-*n*-propyl-carbinyl isocyanate on btg with conc. HCl see (1).]

[For data on density and parachor of  $\bar{C}$  at 0°, 15°, 25°, 50°, and 65° see (6).]

$\bar{C}$  with Mg in dry ether as specified (2) gives 67-78% yield corresponding  $\text{RMgCl}$ .

[ $\bar{C}$  converted as above to  $\text{RMgCl}$ , treated with formaldehyde gas, gives (30% yield (2)) 2-ethyl-2-methylpentanol-1, b.p. 75.5-76.0° at 15 mm.,  $n_D^{20} = 1.4353$  (2).]

$\bar{C}$  with  $\text{C}_6\text{H}_6 + \text{AlCl}_3$  yields (4) 3-methyl-3-phenylhexane, b.p. 110-112° at 15 mm.,  $D_4^{20} = 0.8819$ ,  $n_D^{15} = 1.49951$  (4).

3:7950 (1) Montagne, *Ann. chim.* (10) 13, 125 (1930). (2) Whitmore, Badertscher, *J. Am. Chem. Soc.* 55, 1561, 1565 (1933). (3) Huston, Fox, Binder, *J. Org. Chem.* 3, 253 (1939). (4) Halse, *J. prakt. Chem.* (2) 89, 452-453 (1914). (5) Nasarov, *Ber.* 70, 622 (1937). (6) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* 61, 3108 (1939).

3:7955 1-CHLOROHXANE  
(*n*-Hexyl chloride) $\text{C}_6\text{H}_{13}\text{Cl}$ 

Beil. I - 143

I<sub>1</sub>-(51)I<sub>2</sub>-(109)

B.P.		$D_4^{20} = 0.8784$	(18)	$n_D^{20} = 1.42364$	(1)
135-136°	(1)			1.4200	(4)
134-135° cor.	at 763 mm. (2) (3)	0.8765	(7)	1.41991	(18)
134°	at 759 mm. (18)	0.87551	(8)	1.41944	(6)
134°	at 738 mm. (4)				
133.6-134.4°	(5)				
132.9°	at 764.7 mm. (6)				
132.7-133.3°	(15)				
132-133°	at 760 mm. (7)				

Colorless mobile liq., insol. aq.

[For prepn. of  $\bar{C}$  from hexanol-1 (1:6230) by htg. with fuming HCl in s.t. at 100° (100% yield) see (2); by shaking with HCl +  $\text{ZnCl}_2$  for 2 days (45% yield), with  $\text{PCl}_3 + \text{ZnCl}_2$  (61% yield), with  $\text{PCl}_5 + \text{ZnCl}_2$  (77% yield), or with excess  $\text{SOCl}_2$  (yield: 85-87% (1), 63% (18) see (1) (18)); for prepn. from 1-chlorohexene-2 by cat. reductn. see (9).]

[For formation (besides other products) from *n*-hexane by chlorination see (10) (11) (12) (13); for formation from heavy metal *n*-caproates +  $\text{Cl}_2$  see (14).]

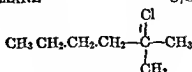
3:7935 (1) Justoni, *Chimica e industria (Italy)* 24, 89-94 (1942); *Cent.* 1943, I 383. (2) Hanriot, Reynaud, *Bull. soc. chim.* (3) 21, 14-15 (1899). (3) Demetre-Vladesco, *Bull. soc. chim.* (3) 6, 834-835 (1891). (4) Justoni, *Chimica e industria (Italy)* 24, 195-201 (1942); *Cent.* 1943, I 1659.

### 3:7945 2-CHLORO-2-METHYLHEXANE

(n-Butyl-dimethyl-carbinyl  
chloride)

 $C_7H_{15}Cl$ 

Beil. I - 156


 $I_1-$ 
 $I_2-$ 

B.P. 135° sl. dec. (1)

$D_4^{25} = 0.8661$  (6)

130-135° sl. dec. (2)

133° dec. at 734 mm. (3)

$D_4^{20} = 0.8608$  (6)  $n_D^{20} = 1.4295$  (6) (3)

132° at 740 mm. (4)

0.863 (3) 1.4202 (5)

69-72° at 90 mm. (5)

58-59° at 50 mm. (8)

39-40° at 20 mm. (4)

35-35.5° at 15.5 mm. (6)

[For prepn. of  $\bar{C}$  from 2-methylhexanol-2 (n-butyl-dimethyl-carbinol) [Beil. I-415, I<sub>2</sub>-(444)] (5) (6) with dry HCl gas at -10° (65-75% yield (6)) or at 10-15° (75% yield (5)) (8), with conc. HCl (1), or with AcCl (1) (2) see indic. refs.; for formn. of  $\bar{C}$  as by-product during reactn. of the above carbinol with  $C_6H_6$  +  $AlCl_3$  (main prod. 45% yield of 2-methyl-2-phenylhexane, b.p. 106-109° at 20 mm.) see (4); for prepn. of  $\bar{C}$  from 2-methylhexanol-3 (isopropyl-n-propyl-carbinol) [Beil. I-415, I<sub>1</sub>-(206)] (3) with dry HCl at 0° (80% yield (3)) by rearrangement see (3).]

[For data on density and parachor of  $\bar{C}$  at 25°, 50°, and 75° see (7).]

$\bar{C}$  with Mg in dry ether as specified (5) gives 74.4% yield corresponding  $RMgCl$ .

$\bar{C}$  converted (as above) to  $RMgCl$  and the latter oxidized with  $O_2$  gives (42% yield (3)) 2-methylhexanol-2, b.p. 139.5-140.5° at 741 mm., 110° at 250 mm.,  $D_4^{20} = 0.813$ ,  $n_D^{20} = 1.4173$  (3).

[For reactn. of  $RMgCl$  with ethyl chloroformate (3:7295) yielding (5) ethyl n-butyl-dimethyl-acetate, b.p. 66.5-70.0° at 16 mm.,  $n_D^{20} = 1.4148$  (5) (corresp. amide, m.p. 92.8-93.8° (5)) see (5); for reactn. of  $RMgCl$  with AcCl (3:7065) giving (9% yield (5)) 3,3-dimethylheptanone-2, b.p. 68-70.5° at 20 mm.,  $n_D^{20} = 1.4206$  (semicarbazone, m.p. 129-130°) (5) see (5).]

$\bar{C}$  converted to  $RMgCl$  and treated with  $CO_2$  gives (5) n-butyl-dimethylacetic acid (constants not given (5)) (corresp. amide via acid chloride, m.p. 92.8-93.8° u.c. (5)).

3:7915 (1) Henry, de Wael, *Bull. acad. roy. Belg.* 1909, 957-963; *Cent.* 1909, I 1854; *Rec. trav. chim.* 23, 448 (1909). (2) Muset, *Bull. acad. roy. Belg.* 1906, 775-789; *Cent.* 1907, I 1313 (3) Whitmore, Johnston, *J. Am. Chem. Soc.* 60, 2266 (1938). (4) Huston, Fox, Binder, *J. Org. Chem.* 3, 252 (1939). (5) Whitmore, Badertscher, *J. Am. Chem. Soc.* 55, 1559-1567 (1933). (6) Whitmore, Woodburn, *J. Am. Chem. Soc.* 55, 363-364 (1933). (7) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* 61, 3105 (1939). (8) Petrov, Kurbaskii, *J. Gen. Chem. (U.S.S.R.)* 14, 492-494 (1944); *C.A.* 39, 4600 (1945).

(1938). (9) Mooradian, Cloke, *J. Am. Chem. Soc.* **68**, 787 (1946). (10) Kleinfeller, *Ber.* **62**, 1595-1598 (1929).

(11) Cloke, Stehr, Steadman, Westcott, *J. Am. Chem. Soc.* **67**, 1588 (1945).

**3:7965** *d,l*- $\alpha,\beta$ -DIMETHYL-*n*-BUTYRYL CHLORIDE  $C_6H_{11}OCl$  Beil. S.N. 162  
(Isopropyl-methyl-acetyl chloride)  $CH_3-CH-CH-C=O$



B.P. 135.9-136.6° at 751 mm. (1)  
38-39° at 18 mm. (2)

$$D_4^{20} = 0.9795 \quad (1)$$

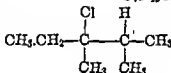
$$D_4^0 = 0.9961 \quad (1)$$

[For prepn. of  $\bar{C}$  from 2,3-dimethylbutanoic acid-1 (1:1114) with  $SOCl_2$  see (1).]

$\bar{C}$  on hydrolysis yields 2,3-dimethylbutanoic acid (1:1114) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to  $\bar{C}$  see 1:1114).

**3:7965** (1) Hommelen, *Bull. soc. chim. Belg.* **42**, 243-250 (1933). (2) Nenitzescu, Chicos, *Ber.* **68**, 1587 (1935).

**3:7970** 3-CHLORO-2,3-DIMETHYLPENTANE  $C_7H_{15}Cl$  Beil. I-157  
(Ethyl-isopropyl-methyl-carbinyl chloride)



B.P. 135-138° at 757 mm. (1)  
133-138° sl. dec. (2)  
41-42° at 20 mm. (3)

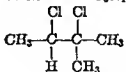
$$D_{23}^{22} = 0.884 \quad (1)$$

$$D_4^0 = 0.899 \quad (1)$$

[For prepn. of  $\bar{C}$  from 2,3-dimethylpentanol-3 (ethyl-isopropyl-methyl-carbinol [Beil. I-417,  $I_1$ -(207),  $I_2$ -(446)] with  $HCl$  (1) or dry  $HCl$  at 0° (50% yield (2)) see (1) (2); for formn. of  $\bar{C}$  from reactn. of the above carbinol with  $C_6H_6 + AlCl_3$  (14% yield accompanied by 22% yield 2,3-dimethyl-2-phenylpentane) see (3).]

**3:7970** (1) Kaschirsky, *J. Russ. Phys.-Chem. Soc.* **13**, 90 (1881); *Ber.* **11**, 985 (1878). (2) Whitmore, Evers, *J. Am. Chem. Soc.* **55**, 813-814 (1933). (3) Huston, Fox, Binder, *J. Org. Chem.* **3**, 253 (1939).

**3:7975** *d,l*-2,3-DICHLORO-2-METHYLBUTANE  $C_6H_{10}Cl_2$  Beil. I-135  
(Trimethylethylene dichloride;  
*ter*-amylene dichloride)



B.P. 137° (1)  
134-138° at 735 mm. (2)  
60° at 60 mm. (11)  
37.0-37.5° at 20 mm. (3)  
35-37° at 18-20 mm. (4)  
33-35° at 17 mm. (5)

$$D_4^{16} = 1.068 \quad (1); \quad n_D^{18} = 1.445 \quad (1)$$

$$1.0696 \quad (3); \quad n_D^{15} = 1.4421 \quad (3);$$

$$n_D^{15} = 1.4566 \quad (3)$$

[For prepn. of  $\bar{C}$  from 2-methylbuten-2 (1) (2) (3) or  $SO_2Cl_2$  at 0° (9) formn. of  $\bar{C}$  low

$\bar{C}$  on refluxing with 10% aq. NaOH yields (9) *n*-hexanol (1:6230).

[For study of reaction of  $\bar{C}$  with KI in acetone see (15); with metallic Na see (16); with  $NaC_2H_5$  see (4); with  $CH_3NH_2$  see (17).]

$\bar{C}$  with Mg in dry ether + trace  $I_2$  gives (97.2% yield (19))  $RMgCl$ .

— *N*-(*n*-Hexyl)tetrachlorophthalimide: lfts. from EtOH, m.p. 150–151° (20). [From  $\bar{C}$  (?) or from *n*-hexyl bromide with K tetrachlorophthalimide (20).]

3:7955 (1) Clark, Streight, *Trans. Roy. Soc. Can.* (3) 23, III, 77–89 (1929). (2) Henry, *Bull. acad. roy. Bel.*

(4) Whitmore

268 (1933).

(7) Olivier, *I*

McNamee, *J. Am. Chem. Soc.* 54, 1649–1651 (1932). (10) Schorlemmer, *Ann.* 161, 272 (1872).

(11) Michael, Turner, *Ber.* 39, 2154–2156 (1906). (12) Ger. 261,577; June 27, 1913; *Cent.*

1913, II 325. (13) Wertyporoch, *Ber.* 66, 732–739 (1933). (14) C. Hunsdiecker, H. Huns-

diecker, Vogt, U.S. 2,176,181, October 17, 1939, *C.A.* 34, 1686 (1940); Brit. 456,565, Dec. 10,

1936, French 803,941, Oct. 12, 1936, *Cent.* 1937, I 2258. (15) Conant, Hussey, *J. Am. Chem.*

*Soc.* 47, 485 (1925). (16) Morton, Hechenbleikner, *J. Am. Chem. Soc.* 58, 1697–1701 (1936).

(17) Westphal, Jerchel, *Ber.* 73, 1007 (1940). (18) Vogel, *J. Chem. Soc.* 1943, 638,640. (19)

Houben, Boedler, Fischer, *Ber.* 69, 1768, 1777 (1936). (20) Allen, Nicholls, *J. Am. Chem. Soc.*

56, 1409–1410 (1934)

3:7960 1,3-DICHLORO-2-METHYLPROPANE  $\begin{array}{c} CH_3 \\ | \\ ClCH_2-C-CH_2Cl \\ | \\ H \end{array}$   $C_4H_8Cl_2$  Beil. I —

$I_1$ —

$I_2$ —(88)

B.P.

136.0° at 760 mm. (1) (2) (3)  $D_4^{20} = 1.131$  (3)  $n_D^{19} = 1.4627$  (4)

135.5°–136.5° (9)

131.5–132.5° at 721 mm. (4)

24.5° at 10 mm. (1)

[For prepn. by chlorination of isobutane see (3) (5) (6); from 3-chloro-2-(chloromethyl)-propene-I (3.5633) or from 1,3-dichloro-2-(chloromethyl)propene-I (3.9066) with  $H_2$  + Pt black in alc. soln. see (10).]

$\bar{C}$  on htg. in s.t. at 180° with anhyd. NaOAc + AcOH yields corresp. diacetate, and this on alcoholysis by htg. with 3% dry HCl in dry MeOH gave an overall yield of 60% of the glycol, 2-methylpropanediol-1,3 [Beil. I-480], b.p. 213–214°,  $D_4^{20} = 1.0290$ ,  $n_D^{20} = 1.4445$  (6).

[For study of further chlorination of  $\bar{C}$  see (7); note that  $\bar{C}$  with  $Cl_2$  or with  $SO_2Cl_2$  +  $H_2O_2$  gives (73% yield (9)) 1,2,3-trichloro-2-methylpropane (3.5385).]

$\bar{C}$  on treatment with Zn dust in 85% alc. gives 38% yield 2-methylpropene-1, (isobutylene) (8).

[ $\bar{C}$  with aq. alc. NaCN as directed (11) gives 20.4% yield  $\gamma$ -chloro- $\beta$ -methyl-*n*-butyronitrile, b.p. 82–83° at 16 mm.,  $D_4^{20} = 1.042$ ,  $n_D^{20} = 1.44255$ , accompanied by 11.5% yield of  $\beta$ -methyl glutaro(di)nitrile, b.p. 133–137° at 16 mm. (11).]

3:7960 (1) Hass, *J. Chem. Education* 13, 493 (1936). (2) Hass, McBee, Weber, *Ind. Eng. Chem.*

27, 1191 (1935). (3) Hass, McBee, Weber, *Ind. Eng. Chem.*

1935; *Cent.* 1936, I 3012

Hass, McBee (to Purdue)

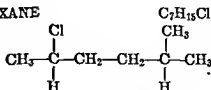
(6) Hass, McBee, Weber

*Soc.* 53, 1027–1029 (1936). (8) Lott, Christiansen, Schakell, *J. Am. Pharm. Assoc.* 27, 125–130

3:7980 (1) Chattaway, Saerens, *J. Chem. Soc.* **117**, 708-711 (1920). (2) Kohlrausch, Sabathy, *Monatsh.* **72**, 307 (1939). (3) Hamilton, Sly, *J. Am. Chem. Soc.* **47**, 436-437 (1925) (4) Carré, *Bull. soc. chim.* (5) **3**, 1069 (1936). (5) Weismann, Garrard, *J. Chem. Soc.* **117**, 328 (1920). (6) Dox, *J. Am. Chem. Soc.* **48**, 1954 (1926).

## 3:7985 5-CHLORO-2-METHYLHEXANE

(Isoamyl-methyl-carbinyl  
chloride)



Beil. I - 156

I<sub>1</sub>—I<sub>2</sub>—

B.P. 138° dec. at 735 mm. (1)  
135-137° (2)

 $D_4^{20} = 0.863$  (1)

[For prepn. of  $\bar{\text{C}}$  from 2-methylhexanol-5 (isoamyl-methyl-carbinol) [Beil. I-416, I-(206), I<sub>1</sub>-(445)] by saturation with dry HCl and stdg. for 6 weeks (90% yield (1)) or htg. in s.t. at 140° (2) see indic. refs.]

$\bar{\text{C}}$  on conversion with Mg in dry ether to RMgCl and treatment with O<sub>2</sub> gives (60% yield (1)) 2-methylhexanol-5, b.p. 151-152° at 736 mm.,  $n_D^{20} = 1.4180$  (*N*-( $\alpha$ -naphthyl)-carbamate), m.p. 84-85° (1).

3:7985 (1) Whitmore, Johnston, *J. Am. Chem. Soc.* **60**, 2267 (1938). (2) Rohn, *Ann.* **190**, 312-313 (1877).

## 3:7988 2-CHLOROHEPTENE-1

 $\text{C}_7\text{H}_{13}\text{Cl}$ 

Beil. S.N. 11

B.P. 138-139° at 748 mm. (1)  
71-72° at 75 mm. (1) (2)

 $D_4^{24} = 0.8788$  (1) $n_D^{24} = 1.4302$  (1) $D_4^{20} = 0.8895$  (2) $n_D^{20} = 1.4340$  (2)

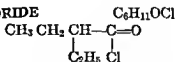
[For prepn. of  $\bar{\text{C}}$  from *n*-amyl methyl ketone (heptanone-2) (1:5460) with PCl<sub>5</sub> in C<sub>6</sub>H<sub>6</sub> (40% yield together with 23% yield 2,2-dichloroheptane (3:9424)) see (2); for prepn. from heptyne-1 (1:8085) + AcCl + SnCl<sub>4</sub> see (2) (both *cis*-4-chlorononen-3-one-2, b.p. 99° at 10 mm.,  $D_4^{25} = 0.9830$ ,  $n_D^{25} = 1.4607$ , and *trans*-4-chlorononen-3-one-2, b.p. 89° at 10 mm.,  $D_4^{25} = 0.9752$ ,  $n_D^{25} = 1.4565$  are also formed (1)).]

$\bar{\text{C}}$  with powdered KOH in mineral oil at 250° does not (2) yield heptyne-1 (dif. from 1-chloroheptene-1 (3:8219)).

3:7988 (1) Kroeger, Sowa, Nieuwland, *J. Org. Chem.* **1**, 163-169 (1936). (2) Bachmann, Hill, *J. Am. Chem. Soc.* **56**, 2730-2732 (1934).

3:7990  $\alpha$ -ETHYL-*n*-BUTYRYL CHLORIDE

(Diethylacetyl chloride)



Beil. II - 334

II<sub>1</sub>—II<sub>2</sub>-(292)

B.P. 138.0-138.8° at 750 mm. (1)  
134-137° (2)  
71° at 88 mm. (3)  
40° at 20 mm. (3)

 $D_4^{20} = 0.9825$  (1) $n_D^{20} = 1.4234$  (3);

1.4239 (3)

 $D_4^0 = 0.9992$  (1)

[For prepn. of  $\bar{\text{C}}$  from 2-ethylbutanoic acid (1:1115) with PCl<sub>5</sub> (2), or with SOCl<sub>2</sub> (1) (85-90% yield (3)) see indic. refs.]

(isopentane) (1:8500) (4) (10) or from 2-chloro-2-methylbutane (*ter*-amyl chloride) (3:7220) (11) with  $\text{Cl}_2$  see indic. refs.; for formn. of  $\tilde{\text{C}}$  from 2-methylbutene-1 (unsym.-ethyl-methyl-ethylene (1:8210) +  $\text{Cl}_2$  see (12); for formn. of  $\tilde{\text{C}}$  from 3-chloro-2-methylbutene-1 (3:7300) +  $\text{HCl}$  see (3); for formn. of  $\tilde{\text{C}}$  from 2-methylbutanol-2 (*ter*-amyl alcohol) (1:6160) +  $\text{Cl}_2$  see (1).]

[ $\tilde{\text{C}}$  on further chlorination yields (3) 2,3,3-trichloro-2-methylbutane (3:4755) together with other prods.]

$\tilde{\text{C}}$  on htg. with solid  $\text{KOH}$  (3) or with alc.  $\text{KOH}$  (3) (4) loses  $\text{HCl}$  yielding 3-chloro-2-methylbutene-2 (3:7335) and other prods. — [ $\tilde{\text{C}}$  on passing over soda-lime or burnt lime at  $600^\circ$  (13) or  $\text{BaCl}_2$  at  $300\text{--}500^\circ$  at 20–50 mm. (14) yields 2-methylbutadiene-1,3 (isoprene) (1:8020).]

$\tilde{\text{C}}$  on boilg. with aq. or with aq.  $\text{Na}_2\text{HPO}_4$  for 30 hrs. gave (2) only 10% hydrolysis;  $\tilde{\text{C}}$  on boilg. with 1 mole  $\text{NaOH}$  in aq. soln. for 24 hrs. gave (2) only 17% hydrolysis, accompanied by isopropyl methyl ketone (1:5410).

$\tilde{\text{C}}$  on boilg. with 35 pts. aq. for 40 hrs. gave (5) complete decomposition with formn. of isopropyl methyl ketone (2-methylbutanone-3) (1:5410) q.v., b.p.  $94^\circ$ .

3:7975 (1) Brochet, *Ann. chim.* (7) 10, 385 (1897). (2) Evers, Rothrock, Woodburn, Stahly, Whitmore, *J. Am. Chem. Soc.* 55, 1137 (1933). (3) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 6,

(4) Ostrowski, *J. Russ. P.* 4, 113 (1905). (5) Badische Anilin- und Soda-Fabrik, Ger. 258,555, 1880; *ibid.* 251,100, June 7, 1902. (6) *Eng. Chem.* 21, 902 (1929). (7) Oct. 28, 1911; *Cent.* 1913, I 1246. (12) 067 (1938); *Cent.* 1939, II 4221; *C.A.* 33, Cent. 1912, I 535. (14) Badische Anilin-1913, I 476.

### 3:7980 *n*-BUTYL CHLOROFORMATE

(*n*-Butyl chlorocarbonate)

$n\text{-C}_4\text{H}_9\text{O CO Cl}$

$\text{C}_5\text{H}_9\text{O}_2\text{Cl}$

Beil. III —

III<sub>1</sub>—

III<sub>2</sub>-(11)

B.P.  $137.8^\circ$  at 734.5 mm. (1)

$D_4^{25} = 1.074$  (1)  $n_D^{18} = 1.4132$  (2)

$137.6^\circ$  at 730 mm. (2)

$142^\circ$  (3)

$n_D^{25} = 1.417$  (1)

$37\text{--}38^\circ$  at 13 mm. (2)

Colorless mobile lachrymatory liq. with sharp but pleasant odor. — Insol. aq. and only slowly hydrolyzed by it even on htg. (1).

[For prepn. (35% yield (3)) from *n*-butyl alc. (1:6180) + phosgene (3:5000) see (1) (3); from di-*n*-butyl carbonate (1:3626) +  $\text{PCl}_5$  see (2).]

$\tilde{\text{C}}$  on htg. with quinoline dec. at  $81^\circ$  (4) into *n*-butyl chloride (3:7160) +  $\text{CO}_2$ .

Ⓐ *n*-Butyl carbamate: from  $\tilde{\text{C}}$  by shaking with conc. aq.  $\text{NH}_4\text{OH}$  (1); pr. from alc., m.p.  $54^\circ$  (1).

Ⓑ *n*-Butyl-*N*-phenylcarbamate (*n*-butyl carbanilate): from  $\tilde{\text{C}}$  in ether by treatment with ether soln. of aniline (1 mole) + pyridine (1 mole) (1); pr., m.p.  $65.5^\circ$  (1),  $61^\circ$  (5). [For corresp. products from many other substituted anilines see (1).]

Ⓒ *n*-Butyl phenylcarbazate: from  $\tilde{\text{C}}$  (3.9 g.) + phenylhydrazine (3.1 g.) + pyridine (3.1 g.) in aq. (15 ml.); after solidification of the sepg. yel. oil it is washed with aq. and recryst. from  $\text{C}_6\text{H}_6$ : white scaly cryst., m.p.  $70^\circ$  (6).

3,5,6-trichloro-2-methylbenzoquinone-1,4 [Beil. VII-651, VII-1-(354)], m.p. 238° (2); from 2,4-dichloro-3-methylphenol (3:1205), from 2,6-dichloro-3-methylphenol (3:0150), and from 4,6-dichloro-3-methylphenol (3:1745) in  $\text{CHCl}_3$  with  $\text{Cl}_2$  see (1).]

[ $\bar{\text{C}}$  with  $\text{PCl}_5$  yields (2) both *tris*-(2,4,6-trichloro-3-methylphenyl) phosphate, m.p. 230° (2), and *bis*-(2,4,6-trichloro-3-methylphenyl) phosphate, m.p. 94.5° (2); for study of Hg, Sb, and Bi derivs. of  $\bar{\text{C}}$  see (2).]

[ $\bar{\text{C}}$  on sulfonation with fuming  $\text{H}_2\text{SO}_4$  (50%  $\text{SO}_3$ ) at 50° yields (4) a monosulfonic acid; for condens. of  $\bar{\text{C}}$  with benzaldehyde-*p*-sulfonic acid and use of prod. as mothproofing agent see (5); for study of use of Na or K salts of  $\bar{\text{C}}$  as wood impregnants (preservatives) see (6).]

$\bar{\text{C}}$  with aqua regia at 100° for 1½ hrs. gives (25% yield (3)) 3,5,6-trichloro-2-methylbenzoquinone-1,4 (see above), m.p. 233° (3).

[ $\bar{\text{C}}$  in aq. alk. with  $\text{Me}_2\text{SO}_4$  yields (2) corresp. methyl ether, ndls. from alc., m.p. 46°, b.p. 258° (2);  $\bar{\text{C}}$  in aq. alk. with  $\text{Et}_2\text{SO}_4$  yields (2) corresp. ethyl ether, ndls. from alc., m.p. 35.5°, b.p. 266° (2) ]

— 2,4,6-Trichloro-3-methylphenyl acetate: m.p. 35°, b.p. 270° (2).

① 2,4,6-Trichloro-3-methylphenyl benzoate: fine prismatic pl. from alc., m.p. 53° (1). [From  $\bar{\text{C}}$  with  $\text{BzCl}$  in pyridine (1).]

② 2,4,6-Trichloro-3-methylphenyl benzenesulfonate: prismatic pl. from alc., m.p. 121° (1). [From  $\bar{\text{C}}$  with benzenesulfonyl chloride in pyridine (1).]

③ 2,4,6-Trichloro-3-methylphenyl *p*-toluenesulfonate: prismatic pl. from alc., m.p. 92-93° (1). [From  $\bar{\text{C}}$  with *p*-toluenesulfonyl chloride in pyridine (1).]

3:0618 (1) Huston, Chen, *J. Am. Chem. Soc.* 55, 4218 (1933). (2) Burřs, *Chem. Listy* 21, 108-114, 148-162, 221-227, 261-265 (1927); *Cent.* 1927, II 1345; *C.A.* 22, 63 (1928). (3) Chulkov, Parini, Barshev, *Org. Chem. Ind (U.S.S.R.)* 3, 410-412 (1937); *Cent.* 1938, II 305; *C.A.* 31, 7047 (1937). (4) Weiler, Better (to I.G.), *Ger.* 557,450, Aug. 24, 1931; *Cent.* 1932, II 2371. (5) Weiler (to I.G.), *Ger.* 548,822, April 20, 1932; *Cent.* 1932, II 799. (6) Iwanowski, et al., *Przemysl Chem.* 16, 205-221 (1932); *Cent.* 1933, I 867; *C.A.* 27, 3796 (1933).

### 3:0625 2,3,6-TRICHLOROTOLUENE



$\text{C}_7\text{H}_5\text{Cl}_3$

Beil. V - 299

V<sub>1</sub>—  
V<sub>2</sub>—

M.P. 45-46° (1)

41-42° (2)

White ndls. from alc.

[For prepn. of  $\bar{\text{C}}$  from 2,6-dichloro-3-aminotoluene [Beil. XII-872] via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reactn. see (1); from *p*-toluenesulfonyl chloride via chlorination, hydrolysis to acid, and subsequent hydrolytic cleavage of the sulfonic acid radical see (3) (2); for formn. of  $\bar{\text{C}}$  together with other prods. from 2,5-dichlorotoluene (3:6245) or 2,6-dichlorotoluene (3:6270) with  $\text{Cl}_2$  in pres. of  $\text{Al/Hg}$  see (4) ]

[ $\bar{\text{C}}$  with  $\text{Cl}_2$  in pres. of  $\text{Al/Hg}$  yields (5) 2,3,5,6-tetrachlorotoluene (3:2575).]

$\bar{\text{C}}$  on mononitration by soln. in cold fuming  $\text{HNO}_3$  yields (1) 2,3,6-trichloro-5-nitrotoluene [Beil. V-333], ndls. from alc., m.p. 57-58° (1);  $\bar{\text{C}}$  on dinitration, e.g., with 6 pts. fuming  $\text{HNO}_3$  + 4 pts. conc.  $\text{H}_2\text{SO}_4$  (1), yields 2,3,6-trichloro-1,5-dinitrotoluene [Beil. V-346], pr. from  $\text{AcOH}$ , m.p. 140-142° (1), 140-141° (6).

$\bar{\text{C}}$  on oxidn. with dil.  $\text{HNO}_3$  in s.t. at 140° yields (1) 2,3,6-trichlorobenzoic acid (3:4500), m.p. 164°.

[ $\tilde{C}$  on htg. with sodium diethylacetate yields (2) corresp. anhydride, b.p. 230° (2).]

[ $\tilde{C}$  with  $Cl_2$  yields (4)  $\alpha$ -chloro-diethylacetyl chloride, b.p. 93° at 70 mm. (amide, m.p. 58° (4));  $\tilde{C}$  with  $Br_2$  yields (5)  $\alpha$ -bromo-diethylacetyl bromide, b.p. 98–100° at 25 mm. (5); for reactn. of  $\tilde{C}$  with  $AlCl_3 + C_6H_6$  see (6).]

[ $\tilde{C}$  (1 mole) upon addition to *ter*-butyl  $MgCl$  (3.7 moles) in dry ether yields (3) (by virtue of reducing actn. of the tertiary  $RMgX$  cpd.) 2-ethylbutanol-1 (1:6223), 2,2-dimethyl-4-ethylhexanol-3 (b.p. 131–132° at 150 mm.,  $D_4^{20} = 0.8339$ ,  $n_D^{20} = 1.4340$ –1.4362,  $N$ -( $\alpha$ -naphthyl)carbamate, m.p. 63–64°, and hexamethylethane (1:7090), m.p. 103° (3).]

$\tilde{C}$  on hydrolysis yields 2-ethylbutanoic acid (1:1115) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to  $\tilde{C}$  see 1:1115).

3:7990 (1) Hommelen, *Bull. soc. chim. Belg.* 42, 243–250 (1933). (2) Freund, Hermann, *Ber.* 23, 189–190 (1890). (3) Whitmore and 11 others, *J. Am. Chem. Soc.* 63, 646, 651–652 (1941). (4) Altwegg, *Pivot*, U.S. 1,493,182, May 6, 1924, *Brit.* 200,706, March 5, 1924, *Cent.* 1924, II 1435, *C.A.* 18, 2053 (1924). (5) Fourneau, Nicolitch, *Bull. soc. chim.* (4) 43, 1238–1239 (1928). (6) Apolit, *Ann. chim.* (10) 2, 80 (1924).



## CHAPTER XVIII

### DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

#### Section 2. $D_4^{20}$ less than 1.1500

(3:8000-3:8499)

3:8000	3-CHLOROBUTANOL-2 ( <i>β</i> -Butylene chlorohydrin; pseudo-butylene chlorohydrin)	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}-\text{CH}_3 \\   \quad   \\ \text{Cl} \quad \text{OH} \end{array}$	$\text{C}_4\text{H}_9\text{OCl}$		Beil. I - 373 I <sub>1</sub> - I <sub>2</sub> -(403)
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B.P. 138-140°	(1)	$D_0^{18} = 1.0692$ (3) (4)	$n_D^{20} = 1.4422$ (9)
138-139° at 763 mm.	(2)		
136.0-137.5° at 760 mm.	(3) (4)		
134-138°	(9)		
76-79° at 100 mm.	(5)		

[See also *d,l*-erythro-3-chlorobutanol-2 (3:8004) and *d,l*-threo-3-chlorobutanol-2 (3:8002).]

$\bar{C}$  in this present discussion designates the ordinary mixture of stereoisomeric configurations of 3-chlorobutanol-2.

Colorless somewhat viscous liq. of agreeable odor. —  $\bar{C}$  is sol. at 20° in 15 vols. aq (2); its sepn. from dilute aq. solns. is best effected by steam distillation at reduced pressure (6) cf. (9).

[For prepn. of  $\bar{C}$  from ordinary butene-2 (mixt. of *cis* and *trans* stereoisomers) by addn. of HOCl (yields: 55% (11), 50% (3), 20% (5)) (4) (1) (2), with  $\text{Cl}_2$  + steam at 100° (60-65%  $\bar{C}$  together with 10-30% 2,3-dichlorobutane (3:7615) (6)), with  $\text{Cl}_2$  + aq. at 40-50° (50-60% yield (6)) (9), or with *N*-chlorourea in dil aq acid 15-17° in pres. of  $\text{CuCl}_2$  (best yield 79.9%  $\bar{C}$  + 20.1% 2,3-dichlorobutane (3:7615) obtd. in 5% AcOH (7), but proportion of the two products varies widely with nature of acid used) see indic. refs.]

[For tabular and graphic data on equilibrium consts. of binary system  $\bar{C}$  + aq., and ternary system  $\bar{C}$  + 2,3-dichlorobutane (3:7615) + aq. see (8).]

$\bar{C}$  in s.t. at 180°, or  $\bar{C}$  with aq. in a.t. at 100° for 10 hrs. or at 120° for 3 hrs., gives (80-100% yield (3)) (10) butanone-2 (ethyl methyl ketone) (1:5405) + HCl (cf. also (14)).

[ $\bar{C}$  with solid KOH (5), or with 40-50% aq. NaOH or KOH (15-20% excess) at 75-90° (11) (10), or with aq. KOH,  $\text{K}_2\text{CO}_3$ , or PbO at ord temp. (3) (4) (2) causes elimination of HCl and gives (yields: 87-90% (11), 75-81% (10), 66% (5)) 2,3-epoxybutane ( $\alpha,\beta$ -dimethylbutylene oxide) (1:6116) (mixt. of *cis* and *trans* stereoisomers) ]

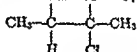
[The simple alkyl ethers of  $\bar{C}$  have been prepared by indirect means; e.g., from butene-2 by action of corresp. alkyl hypochlorites dislvd. in the corresp. alc. or by action of *N,N'*-(3-chloro-2-methoxybutane), b.p. 116°, chloro-2-ethoxybutane, b.p. 122-124°, isopropyl, and isomethyl ethers see (12).]

- 3-Chlorobutyl-2 acetate: b.p. 161-165° at 760 mm., 71-73° at 30 mm.,  $D_4^{20} = 1.0692$ ,  $n_D^{20} = 1.4298$  (13) cf. (7). [Prepd. indirectly from ord. butene-2 with *N,N*-dichlorobenzenesulfonamide + AcOH in ether (28% yield (13)).] [For analogous prepn. of the corresp. formate, chloroacetate, and trichloroacetate see (13).]
- 3-Chlorobutyl-2 benzoate: b.p. 263-265.5 u.c. (7).
- 3-Chlorobutyl-2 *p*-nitrobenzoate: unreported.
- 3-Chlorobutyl-2,3,5-dinitrobenzoate: unreported.

3:8000 (1) Fourneau, Puyat, *Bull. soc. chim.* (4) 31, 427-428 (1922). (2) Henry, *Compt. rend.* 145, 499 (1907). (3) Krassuski, *J. Russ. Phys.-Chem. Soc.* 34, 287-315 (1902); *Cent.* 1902, II 20. (4) Krassuski, *Compt. rend.* 145, 763 (1907). (5) Norton, Hass, *J. Am. Chem. Soc.* 58, 2147 (1936). (6) Batalin, Ugyumov, *J. Gen. Chem. (U.S.S.R.)* 4, 871-874 (1934). *Cent.* 1936, I 986; *C.A.* 29, 2147 (1935). (7) Likhoshesterov, Alekseev, *J. Gen. Chem. (U.S.S.R.)* 3, 927-932 (1933); *Cent.* 1934, II 1437; *C.A.* 28, 3053-3054 (1934). (8) Bushmakín, Gold'man, Kuchinskaya, *Sintet. Kauchuk* 4, No. 1, 33-35 (1935); *Cent.* 1936, I 1131; *C.A.* 29, 4248 (1935). (9) Batalin, Ugyumov, Tikhomirov, *Sintet. Kauchuk* 3, No. 6, 6-12 (1934). *Cent.* 1935, II 1935, not in *C.A.* (10) Batalin, Ugyumov, *Sintet. Kauchuk* 5, No. 6, 8-16 (1936); *Cent.* 1936, II 3357; *C.A.* 30, 6701 (1936).

(11) Wilson, Lucas, *J. Am. Chem. Soc.* 58, 2396-2399 (1936). (12) Likhoshesterov, Alekseev, *J. Gen. Chem. (U.S.S.R.)* 4, 1279-1283 (1934); *Cent.* 1936, I 4287, *C.A.* 29, 3306 (1935). (13) Likhoshesterov, Petrov, *J. Gen. Chem. (U.S.S.R.)* 9, 2000-2008 (1935), *C.A.* 34, 4380-4381 (1940). (14) Gutner, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 6, 1729-1735 (1936), *Cent.* 1937, I 3786; *C.A.* 31, 4265 (1937).

3:8002 *d,l*-threo-3-CHLOROBUTANOL-2 OH H  $C_4H_9OCl$  Beil. S.N. 24



B.P. 130.8°	at 748 mm. (1)	$D_4^{25} = 1.0586$ (1)	$n_D^{25} = 1.4386$ (1)
52.0°	at 30 mm. (1)		
51.5-52.5°	at 30 mm. (2)	$D_4^{20} = 1.0626$ (2)	$n_D^{20} = 1.4403$ (2)
51.0-52.1°	at 30 mm. (1)		

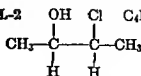
[See also ord. 3-chlorobutanol-2 (3:8000) and *d,l*-erythro-3-chlorobutanol-2 (3:8004).]

[For prepn. of  $\bar{C}$  from *cis*-2,3-epoxybutane (1:6116) (2 moles) with conc. HCl (3 moles) at 5° or below (77% yield) see (1); from *cis*-butene-2 with *ter*-butyl hypochlorite (3:7165) in AcOH/H<sub>2</sub>SO<sub>4</sub> (61% yield (1)) or with Ca(OCl)<sub>2</sub> in AcOH (2) see indic. refs.; from the diacetate of *meso*-butanediol-2,3 (1:6452) in conc. HCl contg. 1 drop conc. H<sub>2</sub>SO<sub>4</sub> with large excess dry HCl gas at -10° for 90 hrs. (43% yield) see (1). — Note that  $\bar{C}$  cannot be obtd. from butene-2 with aq. *N*-chloroacetamide (1).]

[ $\bar{C}$  (1 mole) with SOCl<sub>2</sub> (1.5 moles) refluxed 3 hrs., then kept at 100° for 3 hrs. more, gives (17.4% yield (1)) *d,l*-2,3-dichlorobutane (3:7615); note, however, that  $\bar{C}$  (1 mole) with SOCl<sub>2</sub> (2 moles) htd. 2 hrs. at 95° in pres. of pyridine gives (24% yield (1)) *meso*-2,3-dichlorobutane (3:7580). — Note that  $\bar{C}$  with conc. HCl or with conc. HCl + ZnCl<sub>2</sub> fails to give any dichlorobutane; note also that  $\bar{C}$  fails to react with 60% HBr even in a.t. at 100° for 3 hrs. (1).]

[ $\bar{C}$  with very conc. aq. KOH at 90-95° loses HCl and gives (75% yield (1)) *cis*-2,3-epoxybutane (1:6116).]

3:8002 (1) Lucas, Gould, *J. Am. Chem. Soc.* 63, 2511-2551 (1941). (2) Wilson, Lucas, *J. Am. Chem. Soc.* 58, 2396-2402 (1936).

3:8004 *d,l*-erythro-3-CHLOROBUTANOL-2  $\text{C}_4\text{H}_9\text{OCl}$  Beil. S.N. 24

B.P. 135.4° at 748 mm. (1)  
55.9-56.1° at 30 mm. (1)

 $D_4^{25} = 1.0610$  (1)  $n_D^{25} = 1.4397$  (1)

[See also *ord.* 3-chlorobutanol-2 (3:8000) and *d,l*-threo-3-chlorobutanol-2 (3:8002).]

[For prepn. of  $\bar{C}$  from *trans*-2,3-epoxybutane (1:6116) (2 moles) with conc. HCl (3 moles) at 5° or below (82.5% yield) see (1).]

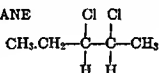
[ $\bar{C}$  (1 mole) with  $\text{SOCl}_2$  (1.5 moles) refluxed 3 hrs., then kept at 100° for 3 more hrs. gives (16% yield (1)) *meso*-2,3-dichlorobutane (3:7580);  $\bar{C}$  (1 mole) in pyridine (2.2 moles) treated with  $\text{SOCl}_2$  (2 moles) at 100° for 3 hrs. gives (63% yield (1)) *d,l*-2,3-dichlorobutane (3:7615), and  $\bar{C}$  (3 moles) with  $\text{PCl}_5$  (1 mole) at 100° for 3 hrs. also gives (20% yield (1)) *d,l*-2,3-dichlorobutane (3:7615); note, however, that  $\bar{C}$  (1 mole) with  $\text{PCl}_5$  (3.9 moles) in  $\text{CHCl}_3$  refluxed 2 hrs. gives (42.7% yield (1)) a mixt. of *d,l*- and *meso*-forms of 2,3-dichlorobutane — Note that  $\bar{C}$  with conc. HCl or with conc. HCl +  $\text{ZnCl}_2$  fails to give any dichlorobutane; note also that  $\bar{C}$  fails to react with 60% HBr even in s.t. at 100° for 3 hrs. (1).]

[ $\bar{C}$  with aq. KOH loses HCl and gives (1) *trans*-2,3-epoxybutane (1:6116).]

3:8004 (1) Lucas, Gould, *J. Am. Chem. Soc.* 63, 2541-2551 (1941).

3:8010 2,3-DICHLOROPENTANE

(*sym.*-Ethyl-methyl-  
ethylene dichloride)

 $\text{C}_5\text{H}_{10}\text{Cl}_2$ 

Beil. I - 131

I<sub>1</sub>—I<sub>2</sub>—(90)

B.P. 138-139.5° (1)  
50-53° at 28 mm. (2)  
50-51° at 20 mm. (3)

Principal component of comml. "amylene dichloride" (5).

[For prepn. of  $\bar{C}$  from pentene-2 (*unsym*-ethyl-methyl-ethylene) (1:8215) +  $\text{Cl}_2$  at -17° (3) or below -5° (4) see indic. refs.; for formn. of  $\bar{C}$  (together with other products) from pentane (1:8505) +  $\text{Cl}_2$  see (2) (5).]

$\bar{C}$  on boilg. with 10% alc. KOH gives (2) 2-chloropentene-2 (3:7285), but  $\bar{C}$  with aq.  $\text{K}_2\text{CO}_3$  gives no pentanediol-2,3 (see below).

$\bar{C}$  on boilg. with Zn dust in alc. or on htg. with Na in xylene at 120° gives (6) pentene-2 (1:8215).

[ $\bar{C}$  + aq. vapor passed at 300° over  $\text{MgCl}_2$  gives (48-50% yield (7)) pentadiene-1,3 (1:8035).]

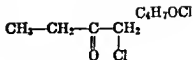
$\bar{C}$  on protracted (250 hrs) boilg. with 35 pts. aq. gives (3) traces of the corresp. glycol, pentanediol-2,3 [Beil. I-482], and either or both pentanone-2 (1:5415) and/or pentanone-3 (1:5420).

3:8010 (1) Kondakov, *Ber.* 24, 931 (1891). (2) Lemke, Tishchenko, *J. Gen. Chem. (U.S.S.R.)*

(3) Froebe, Hochstetter, *Monatsh. J. Gen. Chem. (U.S.S.R.)* 7, 1246-  
*hem.* 21, 902 (1929). (6) Bourgeul,  
170 (1925). (7) Lemke, Tishchenko,

## 3:8012 1-CHLOROBUTANONE-2

(Chloromethyl ethyl ketone)

 $\text{C}_4\text{H}_7\text{OCl}$ 

Beil. I - 669

I<sub>1</sub>-(348)I<sub>2</sub>-(731)

B.P.		B.P. (contd.)	
138.8-139.2° cor. at 755 mm.	(1)	67-68° at 57 mm.	(2) (9)
137-138°	(2) (9)	65° at 50 mm.	(3)
137.5°	(3)	63° at 40 mm.	(10)
135-137°	(4) (5)	59-60° at 30 mm.	(6)
134-136°	(6)	55-56° at 30 mm.	(2)
133-135°	(7)		
125°	at 755 mm. (8)		
124-125°	(11)		

 $D_{15}^{13} = 1.080$  (8) $n_D^{10} = 1.4270$  (8)

[See also 3-chlorobutanone-2 (3:7598).]

Liquid with penetrating odor. — Insol. aq.

[For prepn. of  $\dot{\text{C}}$  from ethyl methyl ketone (butanone-2) (I:5405) with  $\text{Cl}_2$  in pres. of  $\text{CaCO}_3$  + aq. (yields of  $\dot{\text{C}}$  about 25% always accompanied by 75% of the isomeric 3-chlorobutanone-2 (3:7598)) see (1) (3) (6) (10) (12); with  $\text{Cl}_2$  in vapor phase (13) (14), with  $\text{Cl}_2$  or  $\text{SO}_2\text{Cl}_2$  in sunlight (8) (11), or with *N*-chlorosuccinimide (5) see indic. refs. — For formn. of  $\dot{\text{C}}$  from 1-chlorobutan-2-ol (3:8025) by oxidn. with chromic acid (4), from butene-1 with  $\text{HOC}$  (4), from 2-chloromethyl-2-ethyl-4-methyl-1,3-dioxolane-5 by hydrol. with  $\text{AcOH}/\text{HCl}$  (9), or from 2-(chloromethyl)butene-1 (3:9214) by ozonolysis (18) see indic. refs.]

[ $\dot{\text{C}}$  on reduction using yeast gives (15) 1-chlorobutan-2-ol (3:8025).] $\dot{\text{C}}$  on oxidn. with  $\text{HNO}_3$  (8) (11) yields chloroacetic acid (3:1370).

[ $\dot{\text{C}}$  on hydrolysis, e.g., by refluxing overnight with  $\text{K}$  formate in  $\text{MeOH}$ , yields (1) butan-2-ol-1 (propionyl-carbinol) (Beil. I-826, I<sub>2</sub>-(870)), b.p. 153-154°, 50.5-51.0° at 14 mm. (1); note, however, that  $\dot{\text{C}}$  with  $\text{K}$  acetate in  $\text{EtOH}$  gives (6) (8) (11) (65-70% yield (6)) propionyl-carbinyl acetate, b.p. 176° (8) (11), 178-180° (6).]

[ $\dot{\text{C}}$  with conc. aq.  $\text{KCN}$  even in the cold yields (8) (11) the corresp. nitrile, propionyl-acetonitrile (Beil. III-671), b.p. 161-165° (8) (11), colorless liq., insol. aq. —  $\dot{\text{C}}$  with conc. aq.  $(\text{NH}_4)_2\text{SO}_5$  at 70° yields (7) butanone-2-sulfonic acid-1. —  $\dot{\text{C}}$  with  $\text{NaN}_3$  in aq. contg.  $\text{AcOH}$  yields (10) 1-azidobutan-2-ol, oil, b.p. 56° at 2 mm. (10).]

[ $\dot{\text{C}}$  with thiourea refluxed for 2 hrs. gives (72% yield (16)) 2-amino-4-ethylthiazole hydrochloride, cryst. from alc./acetone, m.p. 185.5-187.5° u.c.; this salt with conc. aq.  $\text{NH}_4\text{OH}$  gives the free base, m.p. 35°, b.p. 118-120° at 7 mm. (16) (corresp. acetyl deriv., m.p. 117.5° u.c. (16)). —  $\dot{\text{C}}$  with thiobenzamide +  $\text{NaOAc}$  htd in alc. gives (67% yield (17)) 4-ethyl-2-phenylthiazole, yel. cryst. from xylene, m.p. 117-118° (17).]

$\dot{\text{C}}$  with phenylhydrazine yields (4) a prod., yel. cryst. from  $\text{AcOH}$ , m.p. 210-215° dec., whose structure is in doubt.

① Chloromethyl ethyl ketone semicarbazone: m.p. 121° (5), 120-121° (18).

② Condens. prod. of  $\dot{\text{C}}$  with *N*-methyl- $\beta$ -carbohydrazidopyridinium *p*-toluenesulfonate: cryst. from 1:1  $\text{EtOH}/\text{ether}$ , m.p. 136-137° cor. (19). [From  $\dot{\text{C}}$  + indicated reagent refluxed 15 min. in abs. alc. (19).]

③ 1-(Phthalimido)butanone-2: ndls. from hot aq., m.p. 107° (12). [From  $\dot{\text{C}}$  with  $\text{K}$  phthalimide in dry xylene 2 hrs. at b.p. (27% yield (12)).]

3:8012 (1) Levene, *Haller, J. Biol. Chem.* **76**, 345 (1927). (2) Blaise, *Bull. soc. chim.* (4) **15**, 733 (1914). (3) Juston, *Chimica e industria (Ita.)* **24**, 82-94 (1912); *Cent.* **1913**, 1 343. (4) de

Montmollin, Matile, *Helv. Chim. Acta* 7, 107-109 (1924). (5) Böhl, *Deton. Comm. rend.* 15, 1230 (1911). (6) Kling, *Bull. soc. chim.* (3) 33, 325- (7) Backer, Strating, Zuithoff, *Rec. trav. chim.* 55, *acad. roy. Belg.* 1900, 724-742; *Cent.* 1901, I 95-96. (10) Forster, Fierz, *J. Chem. Soc.* 93, 675, 677 (1908). (11) Henry, *Bull. acad. roy. Belg.* 1900, 57-63; *Cent.* 1900, I 1123. (12) Kolshorn, *Ber.* 37, 2474 (1904). (13) Justoni, *Chimica e industria (Italy)* 24, 195-201 (1942); *Cent.* 1943, I:1659. (14) I.G., French 813,131, May 26, 1937; *Cent.* 1937, II 2071. (15) Santomauro, *Biochem. Z.* 151, 50 (1924); *Cent.* 1924, II 2272. (16) Bergeim, Coy, Lott, *J. Am. Chem. Soc.* 62, 1873 (1940). (17) Friedman, Sparks, Adams, *J. Am. Chem. Soc.* 59, 2203 (1937). (18) Gutner, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1062-1067 (1938); *Cent.* 1939, II 4221. (19) Allen, Gates, *J. Org. Chem.* 6, 596-601 (1941).

## 3:8015 1,1-DICHLOROPENTANE



Beil. S.N. 10



B.P. 139.4-140.2° (1)

[For prepn. of  $\bar{C}$  from isovaleraldehyde (1:0140) with  $PCl_5$  see (1); for formn. of  $\bar{C}$  (together with other prods.) from pentane (1:8505) by vapor-phase photochemical chlorination see (2).]

3:8015 (1) Kohlrausch, Köppl, *Monatsh.* 65, 197 (1935). (2) Hass, Huffman, *J. Am. Chem. Soc.* 63, 1233-1235 (1941).

3:8020 *d,l*- $\alpha$ -METHYL-*n*-VALERYL CHLORIDE

Beil. S.N. 162

(Methyl-*n*-propyl-acetyl chloride)  $CH_3.CH_2.CH_2.CH(CO)CH_3$ 

B.P. 140.0-140.8° at 745 mm. (1)

$D_4^{20} = 0.0781 \text{ (1)}$

$D_4^{20} = 0.9070 \text{ (1)}$

[For prepn. of  $\bar{C}$  from 2-methylpentanoic acid (1:1117) with  $SOCl_2$  see (1).] [The dextrorotatory isomer of  $\bar{C}$  has also been reported (2).]

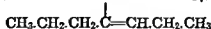
$\bar{C}$  on hydrolysis yields 2-methylpentanoic acid (1:1117) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to  $\bar{C}$  see 1:1117).

3:8020 (1) Hommelen, *Bull. soc. chim. Belg.* 42, 243-250 (1933). (2) Levene, Mikeas, *J. Biol. Chem.* 84, 576 (1929).

## 3:8023 4-CHLOROHEPTENE-3



Beil. I - 220

 $I_1 -$   
 $I_2 - (197)$ 

B.P. 141°

(1)

$D_{20}^{14} = 0.883 \text{ (2)}$

$n_D^{14} = 1.437 \text{ (2)}$

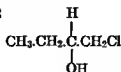
138.5-139.5° cor. (2)

Two geom. stereoisomers of  $\bar{C}$  are possible, but only  $\bar{C}$  has yet been recognized.

[For prepn. of  $\bar{C}$  from heptanone-4 (di-*n*-propyl ketone) (butyrene) (1:5447) with  $PCl_5$  see (1) (2).]

$\bar{C}$  on treatment with  $NaNH_2$  in pseudocumene at 140° yields (3) heptyne-3 (1:8095) together with a solid prod. which with aq. yields (3) heptyne-1 (1:8035).

3:8025 *d,l*-1-CHLOROBUTANOL-2  
( $\alpha$ -Butylene chlorohydrin)

 $\text{C}_4\text{H}_9\text{OCl}$ 

Beil. I —

I<sub>1</sub>—I<sub>2</sub>-(402)

B.P. 141° (1)

68-70° at 27 mm. (2)

53-55° at 17 mm. (5)

52° at 15 mm. (3)

 $D_4^{25} = 1.068$  (2)  $n_D^{25} = 1.4410$  (2) $D_4^{18} = 1.040$  (3)  $n_D^{18} = 1.4353$  (3)

[See also 2-chlorobutanol-1 (3:9160).]

Colorless liq. when freshly distd. but turns red on stdg. and darkens with time (3). — On distn. at ord. press. partially dec. with loss of HCl (3) [and probable formn. of 1,2-epoxybutane (see below)].

[For prepn. of  $\bar{C}$  from butene-1 + HOCl (40-50% yield) see (1) cf. (5); from chloroacetaldehyde (3:7212) +  $\text{C}_2\text{H}_5\text{MgBr}$  in ether see (3) (5); for prepn. (44% yield) by hydrolysis of corresp. trichloroacetate (obtd. by chloration of *sec*.-butyl trichloroacetate) see (2)]

$\bar{C}$  on oxidn. with  $\text{CrO}_3$  yields (1) 1-chlorobutanone-2 (3:8012).

$\bar{C}$  with hot conc. KOH gives (50% yield (1)) 1,2-epoxybutane (1:6118), b.p. 61-62° (4). [For study of this reaction see (4).]

— Chloromethyl-ethyl-carbinyl acetate: unreported.

— Chloromethyl-ethyl-carbinyl benzoate: unreported.

— Chloromethyl-ethyl-carbinyl *p*-nitrobenzoate: unreported.

— Chloromethyl-ethyl-carbinyl 3,5-dinitrobenzoate: unreported.

— 1-(*N*-Phthalimido)butanol-2: unreported.

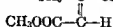
Ⓒ Chloromethyl-ethyl-carbinyl *N*-phenylcarbamate: m.p. 78.5-79° (3).

3:8025 (1) de Montmollin, Matile, *Helv. Chim. Acta* 7, 106-107 (1924). (2) Waddle, Adkins, *J. Am. Chem. Soc.* 61, 3363 (1939). (3) Helferich, Speidel, *Ber.* 54, 2636-2637 (1921). (4) Moureu, Dodé, *Bull. soc. chim.* (5) 4, 288-289 (1937) (5) Olson, Whitacre, *J. Am. Chem. Soc.* 65, 1020 (1943).

3:8028 METHYL  $\beta$ -CHLOROISOCROTONATE

 $\text{C}_5\text{H}_7\text{O}_2\text{Cl}$ 

Beil. II - 417

II<sub>1</sub>-(190)II<sub>2</sub>-(396)

B.P. 142.4° cor. (1)

141-142° (2)

42-43° at 13 mm. (3)

 $D_4^{20} = 1.138$  (1) (3) $D_4^{18.9} = 1.1361$  (3) $D_4^{15} = 1.143$  (1) $n_D^{18.9} = 1.45733$  (3)[See also methyl  $\beta$ -chlorocrotonate (3:9244)]

[For prepn. of  $\bar{C}$  from  $\beta$ -chloroisocrotonic acid (3:1300) in MeOH soln. satd. with HCl gas (1) (3) or htd. with 10% conc.  $\text{H}_2\text{SO}_4$  (yields. 70% (2), 60-62% (4)) see indic. refs.; from  $\beta$ -chloroisocrotonoyl chloride (see under  $\beta$ -chloroisocrotonic acid (3:1300)) with MeOH (yields: 90-95% (4), 80% (2)) see indic. refs.]

[ $\bar{C}$  with NaSH in MeOH gives (40-45% yield (2)) methyl  $\beta$ -mercaptocrotonate; note that the prod. is apparently a mixture of the two geometrically stereoisomeric thioenols together with the keto form, viz., methyl thioacetoacetate,  $\text{CH}_3\text{CSCH}_2\text{COOCH}_3$ ; for details see (2).]

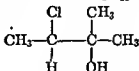
[ $\bar{C}$  with Na salt of ethyl mercaptan below 5° gives (80% yield (4)) a mixt. (b.p. 116-132°

at 14 mm.) of methyl  $\beta$ -ethylmercaptocrotonate and methyl  $\beta$ -ethylmercaptoisocrotonate. —  $\bar{C}$  with Na salt of benzyl mercaptan gives (85% yield (4)) methyl  $\beta$ -benzylmercaptocrotonate, cryst. from ether or MeOH, m.p. 69–70° (4), 73° (2); note the change to the other series of stereoisomers and also that this same prod. is obt'd. (78% yield (2)) from the Na thioenolate of methyl  $\beta$ -mercaptocrotonate with benzyl chloride.

$\bar{C}$  with hydrazine hydrate splits out HCl and MeOH with consequent ring closure yielding (5) (6) 5-methylpyrazolone-3 [Beil. XXIV-19, XXIV<sub>1</sub>-(189)], m.p. 215° (5) (6).

3: 8028 (1) Geuther, Frolich, *Zeit. für Chemie* 1869, 274. (2) Scheibler, Topouzada, Schulze, *J. prakt. Chem.* (2) 124, 16–20 (1930). (3) von Auwers, *Ber.* 45, 2807 (1912). (4) Scheibler, Voss, *Ber.* 53, 381–387 (1920). (5) Freri, *Atti V Congr. nazl. chim. pura applicata, Rome* 1935, Pt. I, 361–365 (1936); *Cent.* 1937, I 4630; *C.A.* 31, 3914 (1937). (6) Freri, *Gazz. chim. ital.* 66, 25 (1936); *Cent.* 1936, II 621; *C.A.* 30, 6387 (1936).

3: 8030 *d,l*-3-CHLORO-2-METHYLBUTANOL-2  $C_4H_9Cl$  Beil. I - 390  
(Trimethylethylene chlorohydrin;  $I_1$ —  
3-chloro-*ter*-amyl alcohol;  $I_2$ -(424)  
 $\alpha$ -chloroethyl-dimethyl-carhinol)



B.P. 141–143° (1)  $D_{25}^{22} = 1.0355$  (2)  
141° (2) (3) (4)  
139–141° (5)  $D_0^0 = 1.0562$  (2)  
43–45° at 15 mm. (5) 1.0546 (1)

Liq. sol. in 15–16 pts. aq. at room temp. (1).

[For prepn. of  $\bar{C}$  from 2-methylbutene-2 (trimethylethylene) (1:8220) with HOCl (50% yield (1) (2)) or with *N*-chlorourea in acid solution (70% yield (5)) see indic. refs.; for prepn. of  $\bar{C}$  from 3-chloropentanone-2 ( $\alpha$ -chloroethyl methyl ketone) (3:7893) (3) (4) or from ethyl  $\alpha$ -chloropropionate (3:8125) (6) with MeMgBr (3) or MeMgI (4) see indic. refs.; note that a mixture of  $\bar{C}$  with 2-chloro-2-methylbutanol-3 (3:9200) results from 2,3-epoxy-2-methylbutane (trimethylethylene oxide) [Beil. XVII-13], b.p. 75°, by ring cleavage with HCl (4).]

$\bar{C}$  on distillation over  $P_2O_5$  (1) or on htg. at 130° with anhydrous oxalic acid (1:0535) (5) or with  $H_2SO_4$  (92% yield (7)) gives 3-chloro-2-methylbutene-2 (trimethylvinyl chloride) (3:7335), b.p. 97–98°, + 1-chloro-2-methylbutene-2 ( $\beta,\gamma$ -dimethylallyl chloride) (3:7485), b.p. 110°.

$\bar{C}$  on hoilg. with aq. +  $BaCO_3$  yields (5) 2-methylbutanediol-2,3 (trimethylethylene glycol) [Beil. I-482,  $I_1$ -(251),  $I_2$ -(549)];  $\bar{C}$  on htg. with KOH (3) (6), alc. KOH (40% yield (5)), or better powdered KOH in ether (70% yield (5)) gives 2,3-epoxy-2-methylbutane (see above).

$\bar{C}$  on htg. in a s.t. with aq. at 140° (8) or by itself at 155° (8), or on htg. with aniline (70% yield (5)), gives 2-methylbutanone-3 (isopropyl methyl ketone) (1:5410).

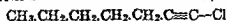
$\bar{C}$  with MeMgI as directed (9) yields 2,3-dimethylbutanol-2 (dimethyl-isopropyl-carhinol) (1:6187).

3: 8031 (1) Geuther, Frolich, *Zeit. für Chemie* 1869, 274. (2) Mokiew-  
sau, Tiffeneau, *Ber.* 53, 381–387 (1920). (3) von Auwers, *Ber.* 45, 2807 (1912). (4) Scheibler, Voss, *Ber.* 53, 381–387 (1920). (5) Freri, *Atti V Congr. nazl. chim. pura applicata, Rome* 1935, Pt. I, 361–365 (1936); *Cent.* 1937, I 4630; *C.A.* 31, 3914 (1937). (6) Freri, *Gazz. chim. ital.* 66, 25 (1936); *Cent.* 1936, II 621; *C.A.* 30, 6387 (1936). (7) Groll, Burgin (to Shell Develop-  
ment Co.), *U.S. Pat.* 2,487,512 (1950). (8) Kras-  
ner, *J. Org. Chem.* 19, 19 (1954). (9) Earl, *J. Proc. Roy. Soc.* 19, 19 (1954).

## 3:8032 1-CHLOROHEPTYNE-1

 $C_7H_{11}Cl$ 

Beil. S.N. 12



B.P. 141-142°	at 760 mm. (1)	$D_4^{24} = 0.9250$ (3)	$n_D^{24} = 1.4411$ (3)
65°	at 49 mm. (2)		
65°	at 45 mm. (3)	$D_4^{18} = 0.918$ (1) (5)	$n_D^{18} = 1.441$ (1) (5)
58.0-58.4°	at 35 mm. (4)		

[For prepn. of  $\bar{C}$  from heptyne-1 (*n*-amylacetylene) (1:8085) via conversion with  $NaNH_2$  in ether (1) or in liq.  $NH_3$  (4) to  $C_6H_{11}C \equiv CNa$  and subsequent reactn. with benzenesulfonyl chloride (yield: 52% (5), 60% (1)) or *p*-toluenesulfonyl chloride (yield: 60-65% (1) (5)) see indic. refs.; via conversion with  $KNH_2$  in liq.  $NH_3$  (3) to  $C_6H_{11}C \equiv CK$  and subsequent treatment with  $Cl_2$  in dry ether at  $-70^\circ$  see (3).]

Refractive indices of  $\bar{C}$  on Pulfrich instrument:  $n_D^{12.9} = 1.4402$ ;  $n_D^{19} = 1.4429$ ;  $n_F^{12.9} = 1.4492$ ;  $n_D^{19} = 1.4540$  (1).

$\bar{C}$  with  $HgSO_4/H_2SO_4$  gives (24-28% yield (1)) 1-chloroheptanone-2, b.p. 72-75° at 20 mm.,  $D_4^{20} = 0.802$ ,  $n_D^{20} = 1.450$  (1) (see, however, different values below).

$\bar{C}$  refluxed 6 hrs. with alc.  $NaOEt$  gives (74% yield (1)) *n*-heptanoic acid (1:1140).

$\bar{C}$  with  $HgO.BF_3$  cat. in  $MeOH$  gives (30% yield (2)) 1-chloro-2,2-dimethoxyheptane, b.p. 80-82° at 8 mm.,  $D_4^{25} = 0.9842$ ,  $n_D^{25} = 1.4325$  (2); this on hydrolysis with 15%  $HCl$  yields (2) 1-chloroheptanone-2, b.p. 80-82° at 13 mm.,  $D_4^{26} = 0.9896$ ,  $n_D^{26} = 1.4387$  (2) (cf. values given above for prepn. by different method.)

$\bar{C}$  with  $KCN$  in aq.  $MeOH$  gives (43% yield (2)) 1-cyano-2-methoxyheptene-1, b.p. 124-131° at 15 mm.,  $D_4^{25} = 0.9205$ ,  $n_D^{25} = 1.4462$  (2) (prob. a mixt. of geom. stereoisomers.)

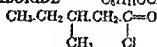
$\bar{C}$  fails to react with  $KI$ ; after bting. 4 hrs. with 10 pts.  $N$   $KI$   $\bar{C}$  was recovered unchanged (1).

3:8032 (1) Truchet, *Ann. chim.* (10) 16, 325, 331-334, 337, 343-351 (1931). (2) Pflaum, Wenzke, *J. Am. Chem. Soc.* 56, 1106 (1934). (3) McCusker, Vogt, *J. Am. Chem. Soc.* 59, 1307-1309 (1937). (4) Cleveland, Murray, Taufen, *J. Chem. Phys.* 10, 173 (1942). (5) Bourgeul, Truchet, *Compt. rend.* 190, 754 (1930).

3:8035 *d,l*-β-METHYL-*n*-VALERYL CHLORIDE $C_8H_{11}OCl$ 

Beil. S.N. 162

(sec.-Butyl-acetyl chloride)



B.P. 142.5-143.0°	at 749 mm. (1)	$D_4^{20} = 0.9781$ (1)
142-144°	(2)	
140°	at 738 mm. (3)	$D_4^{21} = 0.9963$ (1)

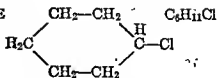
[For prepn. of  $\bar{C}$  from 3-methylpentanoic acid (1:1125) with  $SOCl_2$  see (1) (2) (3).]

$\bar{C}$  with  $AlCl_3 + C_6H_6$  in  $CS_2$  gives (3) (sec.-butyl-acetyl)benzene (β-methyl-*n*-valerophenone, b.p. 160-161° at 50 mm. (semicarbazone, m.p. 179-180°);  $\bar{C}$  with diethyl-zinc yields (2) 3-methylheptanone-5, b.p. 156.5-157.5°,  $D_4^{15} = 0.825$ ,  $n_D^{15} = 1.4159$  (semicarbazone, m.p. 101-102°).]

$\bar{C}$  on hydrolysis yields 3-methylpentanoic acid (1:1125) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to  $\bar{C}$  see 1:1125).

3:8035 (1) Hommelen, *Bull. soc. chim. Belg.* 42, 243-250 (1933). (2) Colonge, *Bull. soc. chim.* (4) 49, 448 (1931). (3) Stenzl, Fichter, *Helv. Chim. Acta* 20, 849 (1937).



**3:8040 CHLOROCYCLOHEXANE**  
 (Cyclohexyl chloride)
C<sub>6</sub>H<sub>11</sub>Cl

Beil. V - 21

V<sub>1</sub>-(8)V<sub>2</sub>-(11)

B.P.		M.P.	
143°	at 768 mm. (1)	-43.9° (4)	$D_4^{20.3} = 1.0000$ (8)
143°	at 760 mm. (34)	-43.0° (7)	$n_D^{20.3} = 1.46264$ (8) (13)
142.9-143.7°	at 760 mm. (2)		$D_4^{12} = 1.0056$ (6)
142.9°	at 760 mm. (3) (4)		$n_D^{20} = 1.4626$ (34)
142°	at 760 mm. (1) (5)		$n_D^{12} = 1.462$ (6)
141.6-142.6° cor.	at 748 mm. (6)		
141-142°	at 741 mm. (1)		
142.03°	at 740 mm. (7)		
66-68°	at 62 mm. (13)		
60.5°	at 48 mm. (3)		
42°	at 21 mm. (3)		
23-24°	at 10 mm. (23)		

Colorless liq. with somewhat penetrating but not disagreeable odor. — Volatile with steam. — Stable when pure and dry; in presence of moisture and traces of HCl, however, turns yellow, then brown (1).

[For prepn. of  $\bar{C}$  from cyclohexanol (1:6415) + conc. HCl under various conditions (yield: 93% (12), 00% (7), 85% (3), 60-70% (0)) see (1) (10) (7) (3) (0); from cyclohexane by chlorination with Cl<sub>2</sub> (11) (1) (6) (18) (33) or with SO<sub>2</sub>Cl<sub>2</sub> (5) (13) see indic. refs.; from cyclohexene (1:8070) with *ter*-BuCl (3:7045) in liq. HF at 0-5° (65% yield) see (34).]

$\bar{C}$  on treatment with alc. KOH (14) (6) (8), or on passing over dehydrohalogenating catalysts such as CaO, BaCl<sub>2</sub>, etc., at elevated temps. (16) (16) (17) (10), or even somewhat on distillation (7), loses HCl to give cyclohexene (1:8070), b.p. 83°.

[For study of behavior of  $\bar{C}$  with AlCl<sub>3</sub> in CS<sub>2</sub> or cyclohexane see (20); for reactn. of  $\bar{C}$  with C<sub>6</sub>H<sub>6</sub> + AlCl<sub>3</sub> to give 60-78% yield of phenylcyclohexane (1:7595), b.p. 233.7°, see (9) (21); for reactn. of  $\bar{C}$  with NaOC<sub>6</sub>H<sub>11</sub> to yield dicyclohexyl ether, b.p. 124-126° at 10 mm., see (22); for study of reactivity of  $\bar{C}$  with KI (23) (24), NaOMe, pyridine, or piperidine (24) see (23) (24); for reactn. of  $\bar{C}$  with oxalyl chloride (3:5060) giving (60% yield (31)) hexahydrobenzoyl chloride (3:8580), b.p. 180-181° u.c., see (31).]

$\bar{C}$  with Mg in dry ether gives under optimum conditions 96.5% yield (25) RMgCl; this on oxidn. with O<sub>2</sub> at 25° gives (81% yield (26)) cyclohexanol (1:6145) q.v., accompanied by small amts. of dicyclohexyl ether and dicyclohexyl (1:8490). [Note that  $\bar{C}$  on reactn. with Ag 3,5-dinitrobenzoate does not (27) yield expected cyclohexyl 3,5-dinitrobenzoate, m.p. 112-113°.]

① Cyclohexanecarboxylic acid (hexahydrobenzoic acid) (1:0575): m.p. 30-31°, b.p. 233°, Neut. Eq. 128. [From RMgCl on treatment with CO<sub>2</sub> and subsequent acidification (85% yield (25) (28)).]

② Cyclohexanecarboxylic acid anilide (hexahydrobenzanilide): m.p. 146° cor. (29), 143-144° u.c. (30). [From RMgCl (30) (or RMgBr (29)) by reactn. with phenyl isocyanate.]

③ Cyclohexanecarboxylic acid *p*-toluidide (hexahydrobenzo-*p*-toluidide): unrecorded.

④ Cyclohexanecarboxylic acid  $\alpha$ -naphthalide (hexahydrobenzo- $\alpha$ -naphthalide): m.p. 183° u.c. (32). [From R.MgBr +  $\alpha$ -naphthyl isocyanate (32).]

3:0625 (1) Cohen, Dakin, *J. Chem. Soc.* 81, 1331-1332 (1902). (2) Austin, Johnson, *J. Am. Chem. Soc.* 54, 658 (1932). (3) Geigy Co., Ger. 210,856, June 18, 1909; *Cent.* 1909, II 79. (4) *Ref.* 1, pp. 1312-1343. (5) Cohen, Dakin, *J. Chem. Soc.* 85, 1284 (1901). (6) Qvist, Holmberg, *Acta Acad. Aboensis Math. Phys.* 6, No. 14, 3-28 (1932); *Cent.* 1932, 2816; *C.A.* 27, 5726-5727 (1933).

### 3: 0655 1,2,3,4-TETRACHLOROBENZENE


 $C_6H_2Cl_4$ 

Beil. V - 204

 $V_1$ —

 $V_2$ -(156)

M.P. 47.5° (4) B.P. 254° cor. at 761.3 mm. (1)

45-46° (1)

45° (2)

44-45° (7)

42.0-43.3° (3)

 Cryst. from  $CCl_4$ ; spar. sol. alc; eas. sol. ether,  $CS_2$ , lgr., or 90% AcOH; sublimes.

[For prepn. of  $\bar{C}$  from 3,5-dichloro-2-nitroaniline [Beil. XII-733] via diazotization and use of  $Cu_2Cl_2$  reactn. (note that the nitro group is also replaced by chloride) in 83% yield (4) see (4) (5); from 2,3,4-trichloroaniline [Beil. XII-626] via diazotization and use of  $Cu_2Cl_2$  reaction see (7) (6) cf. (1); from 1,2,3-trichlorobenzene (3.0990) with  $Cl_2$  in  $CCl_4$  in pres. of Al/Hg see (7), for formn. of  $\bar{C}$  as by-prod. of actn. of conc.  $HNO_3$  on acet-2,4-dichloroanilide see (2).]

[For use of  $\bar{C}$  in mixts. of dielectric liquids see (8).]

[For behavior of  $\bar{C}$  with liq.  $Cl_2$  yielding addn. products see (9).]

[For behavior of  $\bar{C}$  with NaOMe see (4) (10).]

$\bar{C}$  on mononitration by warming with  $HNO_2$  ( $D = 1.52$ ) (1) yields 1,2,3,4-tetrachloro-5-nitrobenzene [Beil. V-247], m p. 64.5° (1), 62.0-63.5° (7), 66-67° (11); this prod. on further nitration by boilg. 2 hrs. with 10 pts. mixed  $HNO_3$  ( $D = 1.52$ ) + conc.  $H_2SO_4$  yields 1,2,3,4-tetrachloro-5,6-dinitrobenzene, m p. 151° (11).

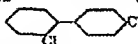
3:0655 (1) Beilstein, Kurbatow, *Ann.* 192, 238-239 (1875). (2) Gotts, Hunter, *J. Chem. Soc.* 125, 447 (1921). (3) Dadiou, Pongratz, Kohlrausch, *Monatsh.* 61, 433 (1932). (4) Holleman, *Rec. trav. chim.* 39, 741-743, 749 (1920). (5) Holleman, van Haften, *Rec. trav. chim.* 40, 70 (1921). (6) Körner, Contardi, *Atti accad. Lincei* 5, 18, 196 (1904). (7) Cohen, Hartley, *J. Chem. Soc.* 87, 1365 (1905). (8) Compagnie Française Thomson-Houston, French 48,584, April 5, 1935; *Cent.* 1935, II 906, *C.A.* 33, 277 (1939). (9) van der Linden, *Rec. trav. chim.* 55, 421-430 (1936). (10) de Crauw, *Rec. trav. chim.* 50, 757 (1931).

(11) Berckmans, Holleman, *Rec. trav. chim.* 44, 856-857 (1925).

### 3: 0670 2,4'-DICHLOROBIPHENYL

 $C_{12}H_8Cl_2$ 

Beil. S.N. 479



M.P. 46° (1) B.P. 191° at 30 mm. (2)

 Cryst. from alc (1); sol. in  $C_6H_6$  or AcOH (1).

[For prepn. of  $\bar{C}$  from 2-amino-4'-chlorobiphenyl (2), from 4-amino-2,4'-dichlorobiphenyl (1), or 2,4'-diaminobiphenyl (1) by appropriate diazo reactions see (1) (2).]

$\bar{C}$  on oxidn. with  $CrO_3$  + AcOH yields (2) p-chlorobenzoic acid (3:4940), m p. 232° (2).

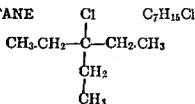
3:0670 (1) Finzi, Bellavita, *Gazz. chim. Ital.* 64, 339 (1934). (2) de Crauw, *Rec. trav. chim.* 50, 776-777 (1931).

(1) (4) (*p*-nitrobenzoate, m.p. 40–41° (2); *N*-(*p*-xenyl)carbamate, m.p. 103.5° (2)) with  $\text{PCl}_5$  (73% yield (4)) (1) (5) or with  $\text{PCl}_3$  + pyridine at 0° (2) see indic. refs.] [The levorotatory isomer of  $\bar{\text{C}}$  (from dextrorotatory hepten-2-ol-4, with  $\text{PCl}_3$  + pyridine at 0° (2)) has b.p. 44° at 14 mm.,  $n_D^{21} = 1.4430$  (2).]

[ $\bar{\text{C}}$  with phenol +  $\text{K}_2\text{CO}_3$  in acetone gives (65% yield (4)) (3) phenyl  $\alpha$ -(*n*-propyl)crotyl ether, b.p. 153–154° at 23 mm. (4), 103–104° at 4 mm. (3),  $D_{20}^{20} = 0.9282$  (3),  $n_D^{21} = 1.5000$  (3). — For studies of the rearr. of this ether on hgt. see (1).] [For similar reaction of  $\bar{\text{C}}$  with *o*-cresol see (3).]

3:8050 (1) Hurd, Williams, *J. Am. Chem. Soc.* 58, 2636–2637 (1936). (2) Arcus, Kenyon, *J. Chem. Soc.* 1938, 1918. (3) Hurd, Puterbaugh, *J. Org. Chem.* 2, 382–384 (1938). (4) Hurd, Cohen, *J. Am. Chem. Soc.* 53, 1920–1922 (1931). (5) Reif, *Ber.* 41, 2743 (1908).

3:8055 3-CHLORO-3-ETHYLPENTANE  
(Triethylcarbinyl chloride)

 $\text{C}_7\text{H}_{15}\text{Cl}$ 

Beil. I —

I<sub>1</sub>-(58)I<sub>2</sub>-(120)

B.P. 143–144°

(1)

 $n_D^{25} = 1.4311$  (3)

140–143°

(2)

 $D_{25}^{25} = 0.8951$  (3)

1.43276 (1)

83–83.5° cor. at 100 mm. (3)

 $n_D^{20} = 1.4329$  (4)

64–65° at 52 mm. (4)

 $D_4^{25} = 0.8644$  (1)

1.4293 (2)

43–44° at 20 mm. (5)

 $n_D^{18} = 1.4310$  (2)

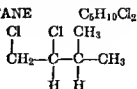
[For prepn. of  $\bar{\text{C}}$  from 3-ethylpentanol-3 (triethylcarbinol) (1:6218) with dry  $\text{HCl}$  at 10–15° (88% yield (4)), with  $\text{HCl}$  (1), or with conc.  $\text{HCl}$  +  $\text{ZnCl}_2$  at room temp. (3) see indic. refs.; for formn. of  $\bar{\text{C}}$  (2% yield (5)) as by-product of reactn. of triethylcarbinol with  $\text{AlCl}_3$  +  $\text{C}_6\text{H}_6$  (main prod. is 40% yield of 3-ethyl-3-phenylpentane, b.p. 225–226° at 745 mm., 107–108° at 20 mm.,  $n_D^{25} = 1.4953$ ,  $n_D^{20} = 1.4975$ ) see (5); for prepn. of  $\bar{\text{C}}$  from 3-ethylpentene-2 (1:8330) with  $\text{HCl}$  gas in  $\text{AcOH}$  (3) or with conc. or fuming  $\text{HCl}$  (2) see (2) (3).]

$\bar{\text{C}}$  with  $\text{Mg}$  in dry ether as directed (4) gives 58% yield corresp.  $\text{RMgCl}$ .

$\bar{\text{C}}$  converted (as above) to  $\text{RMgCl}$ , treated with formaldehyde gas, gives (10% yield (4)) 2,2-diethylbutanol-1, b.p. 75–78° at 12 mm.,  $n_D^{20} = 1.443$  (4).

3:8055 (1) Schreiner, *J. prakt. Chem.* (2) 83, 296 (1910). (2) Nasarov, *Ber.* 70, 623 (1937). (3) Lucas, *J. Am. Chem. Soc.* 51, 252–253 (1929). (4) Whitmore, Badertscher, *J. Am. Chem. Soc.* 55, 1560–1562, 1566 (1933). (5) Huston, Fox, Binder, *J. Org. Chem.* 3, 253 (1939).

3:8075 *d,l*-3,4-DICHLORO-2-METHYLBUTANE  
(Isopropylethylene dichloride)

 $\text{C}_6\text{H}_{10}\text{Cl}_2$ 

Beil. I - 137

I<sub>1</sub>-(47)I<sub>2</sub>—

B.P. 143–145° (1) (3).

142° (2)

[For prepn. of  $\bar{\text{C}}$  from 3-methylbutene-1 (isopropylethylene) (1:8200) +  $\text{Cl}_2$  see (1); for formn. (together with 1,4-dichloro-2-methylbutane (3:8360) and 2,4-dichloro-2-methylbutane (3:8105)) from 4-chloro-2-methylbutane (isoamyl chloride) (3:7365) with  $\text{Cl}_2$  in light see (2) (4).]

- 1929, 502. (10) I Zugravescu, S. Zugravescu, *Bul. Soc. Chim. România* 19-A, 85-92 (1937);  
*Cent.* 1939, II 1279.  
 (11) Nagornov, Rotinyantz, *I* 2648, *C.A.* 21, 3780 (1927).  
 (12) Mailhe, *Ann. chim.* (8) 10, 10, 255, *Bull. soc. chim. Belg.* 48, 255, 1915.  
 (13) Layes, Turner, *J. Chem. Soc.* 1915, 1915.

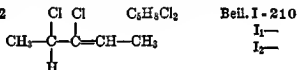
206 (1931).

- (21) Naunhoeffer, *J. prakt. Chem.* (2) 133, 105-107 (1932). (22) Fichter, Siegrist, *Helv. Chim. Acta* 15, 100 (1932).  
 (23) Gilman, Furry, *J. Am. Chem. Soc.* 64, 332 (1941). (24) Zellner (to Tide Water Associated Oil Co.), U.S. 2,370,342, Feb. 27, 1946; *C.A.* 39, 3534 (1945). (25) Simons, Meunier, *J. Am. Chem. Soc.* 65, 1269-1271 (1943).

*Soc.* 56, 2119 (1934).

- (31) Kharasch, Brown, *J. Am. Chem. Soc.* 64, 332 (1941). (32) Gilman, Furry, *J. Am. Chem. Soc.* 50, 1216 (1928). (33) Zellner (to Tide Water Associated Oil Co.), U.S. 2,370,342, Feb. 27, 1946; *C.A.* 39, 3534 (1945). (34) Simons, Meunier, *J. Am. Chem. Soc.* 65, 1269-1271 (1943).

### 3: 8045 *d,l*-3,4-DICHLOROPENTENE-2



B.P. 142-144° at 736 mm. (1)

Two geom. stereoisomers of  $\bar{C}$  are possible, but as yet only this one is recognized.

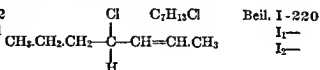
[For prepn. of  $\bar{C}$  from 3-chloropenten-2-ol-4 with  $\text{PCl}_3$  see (1).]

$\bar{C}$  on boilg. with aq. is partially reconverted (1) to 3-chloropenten-2-ol-4 [Beil. I-443], b.p. 158-159° at 724.4 mm

$\bar{C}$  adds  $\text{Br}_2$  yielding (1) 2,3-dibromo-3,4-dichloropentane, b.p. 140-145° at 31 mm. (1).

3: 8045 (1) Garzarolli-Thurnlackh, *Ann.* 223, 160-161 (1884).

### 3: 8050 *d,l*-4-CHLOROHEPTENE-2 (Propenyl-*n*-propyl-carbinyl chloride)



B.P. 140-145° (1)

140-144° (5)

86-90° at 104 mm. (5)

49° at 21 mm. (2)

46-48° at 12 mm. (3)

$n_D^{21} = 1.4430$  (2)

$n_D^{19} = 1.4422$  (3)

$D_4^{18} = 0.879$  (2)

Note that some evidence exists (1) that in certain reactions  $\bar{C}$  reacts (by virtue of allyl transposition) as its synionic isomer 2-chloroheptene-3 (but this has not itself been characterized).

[For prepn. from hepten-2-ol-4 (propenyl-*n*-propyl-carbinol) [Beil. I-447, I<sub>2</sub>(488)]

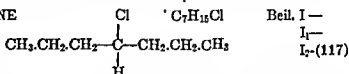
$\bar{C}$  with  $Br_2$  followed by abs. alc. gives (94% yield (6)) ethyl  $\alpha$ -bromo-isobutylacetate, b.p. 100–102° nt 17 mm. (6); for study of catalytic reduction of  $\bar{C}$  see (7).]

$\bar{C}$  on hydrolysis yields isobutylacetic acid (isocaproic acid) (1:1127) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to  $\bar{C}$  see 1:1127).

3:8090 (1) Hommelen, *Bull. soc. chim. Belg.* **42**, 243–250 (1933). (2) Kohlrausch, Pongratz, *Z. physik. Chem. B-22*, 383 (1933). (3) Freundler, *Bull. soc. chim.* (3) **13**, 833 (1895). (4) Clark, Bell, *Trans. Roy. Soc. Can.* (3) **27**, III 07–103 (1933). (5) Curtius, Harnisch, *J. prakt. Chem.* (2) **125**, 194 (1930). (6) Guha, Muthanna, *Ber.* **71**, 2670 (1938). (7) Grignard, Mingasson, *Compt. rend.* **185**, 1173–1176 (1927). (8) Rupe, Giesler, *Helv. Chim. Acta* **11**, 664 (1928).

### 3:8095 *d,l*-4-CHLOROHEPTANE

(Di-*n*-propyl-carbinyl chloride)



B.P. 144–145° at 758 mm. (1)

$D_4^{20} = 0.8710$  (3)  $n_D^{20} = 1.4237$  (1)

143.1–144.4° at 751 mm. (2)

0.8619 (1) 1.4231 (3)

48.9° at 21 mm. (3)

$D_4^{15} = 0.8751$  (3) 1.4199 (2)

[For prepn. of  $\bar{C}$  from heptanol-4 (1:6228) with conc.  $HCl + ZnCl_2$  (1) (2) (3) (yield: 60–64% (3), 35% (1)) see indic. refs.]

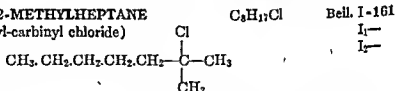
$\bar{C}$  converted to corresp. acetate by 7-hr. reflux with  $KOAc + AcOH$ , then hydrolyzed by 6-hr. boilg. with 20% alc.  $KOH$ , and the resultant heptanol-4 (1:6228) oxidized with  $CrO_3/H_2SO_4$  gives (3) heptanone-4 (1:5447) q.v. (semicarbazone, m.p. 129° by this route, 132° from authentic heptanone-4 (3)).

$\bar{C}$  with powdered or alc.  $KOH$  or  $NaOH$  slowly regenerates heptanol-4 (1:6228) without any trace of olefin (1).

3:8095 (1) Mathus, Gibon, *Bull. soc. chim. Belg.* **34**, 306 (1925). (2) Dillon, Lucas, *J. Am. Chem. Soc.* **50**, 1711–1714 (1928). (3) Sherrill, *J. Am. Chem. Soc.* **52**, 1985–1989 (1930).

### 3:8100 *d,l*-2-CHLORO-2-METHYLHEPTANE

(*n*-Amyl-dimethyl-carbinyl chloride)



B.P. 140–150° dec. (1)

$D_4^{25} = 0.8568$  (2)  $n_D^{25} = 1.4363$  (4)

49.5–51° at 15 mm. (2)

$n_D^{20} = 1.4263$  (4)

1.4257 (3)

1.4250 (2)

$\bar{C}$  decomposes very easily on distn. (cf. (3)).

[For prepn. of  $\bar{C}$  from 2-methylheptanol-2 (*n*-amyl-dimethyl-carbinol) [Beil. I-420, I<sub>1</sub>-(209), I<sub>2</sub>-(452) (2) (3)] with  $HCl$  gas (yield 81% (2), 73% (3)) or with  $AcCl$  (1) see indic. refs.]

$\bar{C}$  on distn. over powdered  $KOH$  gives 2-methylheptene-2 ( $\alpha,\alpha$ -dimethyl- $\beta$ -*n*-butyl-ethylene) [Beil. I-222, I<sub>1</sub>-(93)], b.p. 122–123° nt 755 mm.,  $D_4^{20} = 0.816$  (1).

$\bar{C}$  with  $Mg$  in dry ether as directed (2) gives 59.9% yield  $RMgCl$ .

$\bar{C}$  on conversion to  $RMgCl$  and subsequent treatment with  $CO_2$  gives (in addition to much olefin) (22% yield (2)) dimethyl-*n*-amyl-acetic acid, b.p. 118°,  $n_D^{20} = 1.4335$ –1.4305 (2) (amide, m.p. 102.5–103.5° (2)).

$\bar{C}$  is scarcely attacked by  $K_2CO_3$  (1) —  $\bar{C}$  on boilg. with aq. for 100 hrs. can be recovered unchanged to extent of 85%, the remainder yielding traces of 2-methylbutanediol-1,2 [Beil. I-482], 2-methylbutanone-3 (isopropyl methyl ketone) (1:5410), and 2-methyl butyne-1 (isopropylacetylene) (1:8010) (3).

$\bar{C}$  passed over soda-lime at  $470^\circ$  gives (2) 2-methylbutadiene-1,3 (isoprene) (1:8020).

3:8075 (1) Kondakow, *J. Russ. Phys.-Chem. Soc.* 20, 144 (1888). (2) Perkin, *J. Soc. Chem. Ind.* 31, 616-624 (1912). (3) Froebe, *Hochstetter, Monatsch.* 23, 1079-1081 (1902). (4) Badische Anilin- u. Soda-Fabrik, Ger. 261,677, March 14, 1911; *Cent.* 1913, II 325.

### 3:8080 *d,l*-3-CHLOROHEPTANE

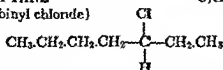
(Ethyl-*n*-butyl-carbinyl chloride)

$C_7H_{15}Cl$

Beil. I —

I<sub>1</sub>—

I<sub>2</sub>-(117)



B.P.  $143.4-144.4^\circ$  at 751 mm. (1)

$D_4^{20} = 0.8690$  (2)  $n_D^{20} = 1.4237$  (1)

$48.3^\circ$  at 21 mm. (2)

$D_4^{15} = 0.8732$  (2)  $1.4228$  (2)

[For prepn. of  $\bar{C}$  from heptanol-3 [Beil. I<sub>1</sub>-(205), I<sub>2</sub>-(444) (2)] with conc. HCl +  $ZnCl_2$  (yield 60-64% (2)), 30% (1)] see (1) (2).] [A dextrorotatory form of  $\bar{C}$  has been prepd. (3) by cat. hydrogenation of levorotatory 3-chloroheptene-1: b.p.  $87-90^\circ$  at 113 mm.,  $n_D^{25} = 1.4221$  (3)]

$\bar{C}$  converted to corresp. acetate by 7 hrs. reflux with KOAc + AcOH, then hydrolyzed by 6 hrs. boilg. with 20% alc. KOH, and the resultant heptanol-3 oxidized with  $CrO_3/H_2SO_4$  gives (2) heptanone-3 [Beil. I-699, I<sub>1</sub>-(359), I<sub>2</sub>-(754)] (semicarbazone, m.p.  $88-89^\circ$  (2)).

3:8080 (1) Dillon, Lucas, *J. Am. Chem. Soc.* 50, 1711-1714 (1928). (2) Sherrill, *J. Am. Chem. Soc.* 52, 1985-1988 (1930). (3) Levene, Rothen, *J. Biol. Chem.* 119, 191-192 (1937).

### 3:8085 4-CHLOROHEPTADIENE-1,6

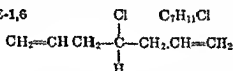
(Diallylcarbinyl chloride)

$C_7H_{11}Cl$

Beil. I-257

I<sub>1</sub>—

I<sub>2</sub>—



B.P.  $144^\circ$  dec. (1)

[For prepn. of  $\bar{C}$  from heptadien-1,6-di-ol-4 (diallylcarbinol) [Beil. I-455, I<sub>2</sub>-(506)] with  $PCl_3$  see (1)]

$\bar{C}$  with alc. KOH readily removes 1 HCl yielding a heptatriene, b.p.  $115^\circ$  (1).

3:8085 (1) Saytzeff, *Ann.* 189, 141-145 (1877).

### 3:8090 $\gamma$ -METHYL-*n*-VALERYL CHLORIDE

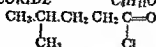
(Isocaproyl chloride,  
isobutyl-acetyl chloride)

$C_6H_{11}OCl$

Beil. II - 329

II<sub>1</sub>—

II<sub>2</sub>-(289)



B.P.  $143.8-144.6^\circ$  at 745 mm. (1)

$D_4^{20} = 0.9725$  (1)

$141.9-144.7^\circ$  (2)

$141-142^\circ$  (3)

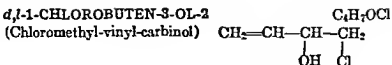
$D_4^0 = 0.9922$  (1)

$[129-130^\circ$  (8)]

[For prepn. of  $\bar{C}$  from 4-methylpentanoic acid-1 (isocaproic acid) (1:1127) with  $PCl_3$  (63% yield (4)), with  $PCl_3 + ZnCl_2$  (68% yield (4)), or with  $SOCl_2$  (1) (2) (5) (8) (82% yield (4)) see indic. refs.]

3:8110 *d,l*-1-CHLOROBUTEN-3-OL-2

(Chloromethyl-vinyl-carbinol)



Beil. S.N. 25

B.P.

144-147° (1)

 $D_4^{20} = 1.111$  (3) $n_D^{20} = 1.4660$  (3)

76° at 60 mm. (2)

1.4643 (2)

64.0-64.8° at 30 mm. (3)

 $D_4^{15} = 1.1214$  (1) $n_D^{15} = 1.468$  (1)

[See also 2-chlorobuten-3-ol-1 (3:9113).]

[For prepn. of  $\bar{C}$  from butadiene-1,3 with HOCl generated from  $\text{Ca}(\text{OCl})_2 + \text{CO}_2$  (3) or from *N*-chlorourea + acid in cold (1) (yields of  $\bar{C}$ : 75% (1), 52% (3)) see indic. refs.]

$\bar{C}$  with  $\text{Br}_2$  in  $\text{CHCl}_3$  adds 1 mole halogen giving (1) 1-chloro-3,4-dibromobutanol-2, h.p. 129-130° at 10 mm.;  $D_4^{20} = 2.042$ ,  $D_4^{15} = 2.0504$ ;  $n_D^{20} = 1.561$ ,  $n_D^{15} = 1.564$  (1); note that this prod. on oxidn. with  $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$  at 35° gives (1) 1-chloro-3,4-dibromobutanone-2, h.p. 132-133° at 25 mm.;  $D_4^{20} = 2.0521$ ,  $D_4^{15} = 2.0589$ ;  $n_D^{20} = 1.554$ ,  $n_D^{15} = 1.559$  (1).

$\bar{C}$  with 50% aq. NaOH at 115-135° for 1 hr. (3) or with 60% KOH (1) loses HCl ring closing to (yields: 87% (2), 84% (3)) 3,4-epoxybutene-1, h.p. 65.0-65.8° at 739 mm,  $D_4^{20} = 0.875$ ,  $n_D^{20} = 1.4170$  (3) cf. (1). [For various reactions of this product see (1) (2) (3) (4).]

[For study of rate of hydrolysis of  $\bar{C}$  with aq. NaOH see (2).]

— 1-Methoxybuten-3-ol-2 ( $\bar{C}$  methyl ether): h.p. 143-144° (1) (4), 69-71° at 49 mm. (3);  $D_4^{20} = 0.9470$  (1) (4);  $n_D^{20} = 1.4343$  (1) (4), 1.4297 (3); corresp. 3,5-dinitrobenzoate, m.p. 70-71° (3). [From  $\bar{C}$  (3) or from 3,4-epoxybutene-1 (above) (1) (4) with MeOH/NaOMe in 51-52% yields (3) (1).]

— 1-Ethoxybuten-3-ol-2 ( $\bar{C}$  ethyl ether): h.p. 153-157°;  $D_4^{15} = 0.9214$ ;  $n_D^{15} = 1.4330$  (1) (4). [Presumably from  $\bar{C}$  (although not actually reported) or from 3,4-epoxybutene-1 (above) (1) (4) with EtOH/NaOEt.]

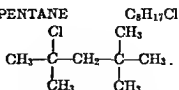
— 1-Chlorobuten-3-yl-2 acetate: b.p. 163-166°;  $D_4^{15} = 1.1308$ ;  $n_D^{15} = 1.4610$  (1).

⑧ 1-Chlorobuten-3-yl-2 3,5-dinitrobenzoate: m.p. 61.5-63.5° u.c. (3). [Note that this prod. depresses m.p. of corresp. deriv. (m.p. 65.5° u.c.) from 2-chlorobuten-3-ol-1 (3:9113).]

3:8110 (1) Petrov, *J. Gen. Chem. (U.S.S.R.)* 8, 131-140 (1938); *Cent.* 1939, I 2596; *C.A.* 32, 5369 (1938). (2) Kadesch, *J. Am. Chem. Soc.* 68, 45-48 (1946). (3) Kadesch, *J. Am. Chem. Soc.* 68, 41-45 (1946). (4) Petrov, *Acta Univ. Voronegiensis* 8, No. 2, 71-79 (1935); *Cent.* 1936, II 2333-2334; *C.A.* 32, 4524 (1938).

## 3:8113 4-CHLORO-2,2,4-TRIMETHYLPENTANE

(Di-isobutylene hydrochloride)



Beil. I-164

I<sub>1</sub>-I<sub>2</sub>-

B.P.

145-150° dec. (1)

M.P.

-26° (4)

 $D_4^{18} = 0.8756$  (2) $n_D^{24} = 1.4286$  (6)

62.8° at 40 mm. (6)

44° at 16 mm. (5)

 $D_4^0 = 0.8891$  (2) $n_D^{20} = 1.4307$  (5)

40° at 13 mm. (2)

3:8100 (1) Muset, *Bull. acad. roy. Belg.* 1906, 775-789; *Cent.* 1907, I 1313; *C.A.* 1, 1696 (1907).  
 (2) Whitmore, Badertscher, *J. Am. Chem. Soc.* 55, 1559-1567 (1933). (3) Whitmore, Williams,  
*J. Am. Chem. Soc.* 55, 409 (1933). (4) Smart, Quayle, *J. Am. Chem. Soc.* 67, 21-23 (1945).

3:8103 METHYL  $d,l$ - $\alpha$ -CHLORO- $n$ -BUTYRATE  $C_5H_9O_2Cl$  Beil. II - 277  
 $CH_3CH_2CH(Cl)COOCH_3$   $H_I$ —  
 $Cl$   $H_X$ —

B.P. 145-146° at 766 mm. (1)

$D_4^{25} = 1.0979$  (1)  $n_D^{25} = 1.42526$  (1)

[For prepn. of  $\bar{C}$  from  $\alpha$ -chloro- $n$ -butyronitrile with MeOH + HCl see (1).] For the amide corresp. to  $\bar{C}$  see  $\alpha$ -chloro- $n$ -butyric acid (3:9130).

3:8103 (1) Henry, *Bull. acad. roy. Belg.* (3) 35, 507-520 (1898); *Cent.* 1898, I 273.

3:8105 2,4-DICHLORO-2-METHYLBUTANE  $C_5H_{10}Cl_2$  Beil. I - 135  
 (Isoprene bis-hydrochloride)  $Cl$   $Cl$   $I_1$ -(47)  
 $CH_2-CH_2-C-CH_3$   $I_2$ —  
 $CH_3$

B.P. 145-146° (1)

$D_4^{20} = 1.0654$  (1)  $n_D^{20} = 1.44549$  (5)

144-148° (5)

142° (2)

52-53° at 12 mm. (1)

39° at 10 mm. (5)

[Earlier work on this compd. seems now to have been carried out on impure material and should be disregarded.]

[For prepn. of  $\bar{C}$  from 4-chloro-2-methylbutene-2 (isoprene monohydrochloride) (3:7465) with conc. HCl satd. with HCl gas see (1) (5); for prepn. of  $\bar{C}$  from 2-methylbutadiene-1,3 (isoprene) (1.8020) with conc. HCl see (2) (5); for formn. of  $\bar{C}$  from 2-methylbutane (isopentane) (1.8500) (together with 2,3-dichloro-2-methylbutane (3.7975) and 1,4-dichloro-2-methylbutane (3.8360)) see (3), for formn. of  $\bar{C}$  (together with 1,4-dichloro-2-methylbutane (3.8360) and 3,4-dichloro-2-methylbutane (3.8075)) from 4-chloro-2-methylbutane (isocamyl chloride) (3.7365) +  $Cl_2$  in light see (4)]

$\bar{C}$  on hydrolysis with boilg. 20%  $K_2CO_3$  (3) or 20% aq. NaOH (5) gives 2-methylbutane-diol-2,4 (Beil. I-483, I<sub>1</sub>-(251)), b.p. 105° at 16-17 mm.,  $D_4^{20} = 0.9852$ ,  $n_D^{20} = 1.4434$  [*N,N*-bis (phenylcarbamate), m.p. 113.8-114.6°] (3) cf. (5).

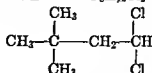
$\bar{C}$  on oxido. with  $KMnO_4$  yields (3)  $\beta$ -hydroxyisovaleric acid [Beil. III-327, III<sub>1</sub>-(122)].

3:8105 (1) Aschan, *Ber.* 51, 1307 (1918). (2) Ostromuiskii, *J. Russ. Phys.-Chem. Soc.* 47, 1983-1988 (1915), *Cent.* 1915, II 307, *C.A.* 10, 1341 (1916). (3) Davydova, Papkina, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 7, 1992-1994 (1937); *Cent.* 1939, I 2397; *C.A.* 32, 482 (1938). (4) Perkin, *J. Soc. Chem. Ind.* 31, 616-624 (1912). (5) Soday (to United Gas Improvement Co.), U.S. 2,376,396, May 22, 1945; *C.A.* 39, 3545-3549 (1945).



(21) Drushel, *Am. J. Sci.* (4) **34**, 69-74 (1912); *Cent.* 1912, II 704; *C.A.* 6, 2593 (1912). (22) Bolin, *Z. anorg. allgem. Chem.* **177**, 246-248 (1929).

3:8132 4,4-DICHLORO-2,2-DIMETHYLBUTANE  $\text{C}_6\text{H}_{12}\text{Cl}_2$  Beil. S.N. 10  
(1,1-Dichloro-3,3-dimethylbutane)



B.P.

M.P.

148° (1)

-56.5°/-56.0° (1)

 $D_4^{20} = 1.0262$  (1) $n_D^{20} = 1.4389$  (1)

[For prepn. of  $\bar{\text{C}}$  from vinyl chloride (3:7010) with 2-methylbutane (isobutane) +  $\text{AlCl}_3$  at  $-10^\circ$  (40% yield) or with *ter*-butyl chloride (3:7045) see (1).]

$\bar{\text{C}}$  with aq. in s.t. at  $300^\circ$  hydrolyzes to *ter*-butylacetaldehyde, b.p.  $102-103^\circ$  (corresp. methone, m.p.  $162-163^\circ$ ; corresp. 2,4-dinitrophenylhydrazones, m.p.  $146-147^\circ$ ) (1).

3:8132 (1) Schmerling, *J. Am. Chem. Soc.* **67**, 1438-1441 (1945).

3:8140 *d,l*-1,2-DICHLOROPENTANE  $\text{C}_5\text{H}_{10}\text{Cl}_2$  Beil. I—  
 $\text{CH}_3\text{CH}_2\text{CH}_2-\text{C}-\text{CH}_2$   $\text{I}_1-$   
 $\quad \quad \quad | \quad |$   $\text{I}_2$ -(95)  
 $\quad \quad \quad \text{H}$

B.P. 148.4-148.8°

(1)

 $D_{25}^{25} = 1.0773$  (2) $n_D^{25} = 1.4453$  (2)

146.0-146.2°

(2)

1.0667 (2)

1.4448 (2)

145.8-146.2° at 739 mm. (2)

58-59°

at 28 mm. (3)

 $D_4^{20} = 1.0872$  (1) $n_D^{20} = 1.4485$  (1)

Colorless oil, insol. aq., volatile with steam.

[For prepn. of  $\bar{\text{C}}$  (70% yield (2)) from 1-chloropentanol-2 (3:8225) with  $\text{SOCl}_2$  + diethylaniline or from pentene-1 (1:8205) in  $\text{CCl}_4$  at  $0^\circ$  +  $\text{Cl}_2$  (50% yield (2)) (1) see (1) (2).]

[For formn. of  $\bar{\text{C}}$  (together with other prods.) from pentane (1:8505) (3) or from 1-chloropentane (3:7460) (4) with  $\text{Cl}_2$  see indic. refs.]

$\bar{\text{C}}$  with alc. KOH gives (3) 1-chloropentene-1 (3:7420), but  $\bar{\text{C}}$  with  $\text{K}_2\text{CO}_3$  does not (3) yield the corresp. glycol.

3:8140 (1) Tishchenko, Shehigel'skaya, *J. Gen. Chem. (U.S.S.R.)* **7**, 1246-1248 (1937); *Cent.* 1938, II 2576; *C.A.* **31**, 6189 (1937). (2) Koelsch, McElvain, *J. Am. Chem. Soc.* **51**, 3393-3394 (1929). (3) Lemke, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **7**, 1995-1998 (1937); *Cent.* 1939, I 2398; *C.A.* **32**, 482 (1938). (4) Hass, Huffman, *J. Am. Chem. Soc.* **63**, 1233-1235 (1941).

3:8144 *d,l*- $\alpha$ -CHLORO-ISOVALERYL CHLORIDE  $\text{C}_6\text{H}_9\text{OCl}_2$  Beil. II-316  
( $\alpha$ -Chloro- $\beta$ -methyl-*n*-butyryl chloride)  $\text{CH}_3-\text{CH}-\text{CH}-\text{C}=\text{O}$   $\text{H}_1-$   
 $\quad \quad \quad | \quad | \quad |$   $\text{H}_2-$   
 $\quad \quad \quad \text{CH}_3 \quad \text{Cl} \quad \text{Cl}$

B.P. 148-149° (1)

 $D^{132} = 1.135$  (1)

[For prepn. of  $\bar{\text{C}}$  from  $\alpha$ -chloro-isovaleric acid (3:0050) with  $\text{PCl}_3$  see (1).]

$\bar{\text{C}}$  on hydrolysis with aq. yields  $\alpha$ -chloro-isovaleric acid (3:0050).

3:8144 (1) Servais, *Rec. trav. chim.* **20**, 53 (1901).

Colorless mobile liq. with characteristic odor.

[For prepn. from 2,4,4-trimethylpentene-1 (1:8340) or 2,4,4-trimethylpentene-2 (1:8345) ("diisobutylene") with conc. HCl (satd. at  $-20^\circ$ ) in s.t. at  $100^\circ$  (1) (2), with HCl gas in cold (5) or at  $-10^\circ$  to  $-25^\circ$  in pres. of  $\text{ZnCl}_2$  (4) (almost quant. yield (5)) see indic. refs.]  $\bar{C}$  on distillation loses HCl and regenerates "diisobutylene" (4) (2).

$\bar{C}$  with alc. KOH yields diisobutylene (see above).

[For reactn. of  $\bar{C}$  with phenol + alc.  $\text{NaOC}_6\text{H}_5$  yielding phenyl diisobutyl ether, b.p.  $250-260^\circ$  see (3); note, however, that this prod. in s.t. at  $250^\circ$  for 2 hrs. rearr. to *p*-(diisobutyl)phenol, m.p.  $84^\circ$  (3).]

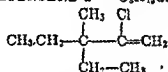
[For reaction of  $\bar{C}$  with  $(\text{CH}_3)_2\text{Zn}$  yielding 2,2,4,4-tetramethylpentane (1:8045), b.p.  $122.3^\circ$ ,  $n_D^{25} = 1.4051$ , see (4).]

[For reactn. of  $\bar{C}$  with silver cyanate, followed by alk. hydrolysis to yield 4-amino-2,2,4-trimethylpentane (acetyl deriv., m.p.  $93^\circ$ ; reactn. prod. with phenyl isocyanate, m.p.  $137^\circ$ ) see (5).]

[ $\bar{C}$  with 2-methyl butane (isopentane) (1:8500) +  $\text{AlCl}_3$  shaken for 2 min. gives (6) 2-chloro-2-methylbutane (*ter*-amyl chloride) (3 7220).]

3:8113 (1) Butlerow, *Ann.* 189, 51-53 (1877). (2) Kondakov, *J. Russ. Phys.-Chem. Soc.* 28, 790 (1896), *J. prakt. Chem.* (2) 54, 449-450 (1896) (3) Natelson, *J. Am. Chem. Soc.* 56, 1585 (1931). (4) Howard, *J. Research Natl. Bur. Standards* 24, 678-679, 681 (1940). (5) Whitmore, Wilson, Capinola, Tongberg, Fleming, McGrew, Cosby, *J. Am. Chem. Soc.* 63, 2041 (1941). (6) Bartlett, Condon, Schneider, *J. Am. Chem. Soc.* 66, 1537 (1944).

3:8115 2-CHLORO-3-ETHYL-3-METHYLPENTENE-1  $\text{C}_8\text{H}_{15}\text{Cl}$  Beil. S.N. 11



B.P.  $147^\circ$  at 743 mm. (1)

$53^\circ$  at 20 mm. (1)

$D_4^{20} = 0.9147$  (1)

$n_D^{25} = 1.4450$  (1)

[For prepn. of  $\bar{C}$  from 3-ethyl-3-methylpentanone-2 [Beil. I-7(760)] (1) with  $\text{PCl}_5$  (65% yield) see (1).]

$\bar{C}$  with  $\text{NaNH}_2$  in mineral oil at  $160-165^\circ$  gives 45% yield 3-ethyl-3-methyl-pentyne-1, b.p.  $93-100^\circ$  at 745 mm.,  $D_4^{20} = 0.7360$ ,  $n_D^{20} = 1.4102$  (Ag salt, darkens  $167^\circ$ , melts  $191.5^\circ$ ) (1).

3:8115 (1) Davis, Marvel, *J. Am. Chem. Soc.* 53, 3844-3845 (1931).

3:8117  $\alpha$ -CHLOROCROTONALDEHYDE

(2-Chlorobuten-2-al-1)

$\text{C}_4\text{H}_5\text{OCl}$

Beil. I - 731



I<sub>1</sub>—



I<sub>2</sub>-(780)

B.P.  $147-150^\circ$  at 760 mm. (1)

$147-140^\circ$  (2)

$147^\circ$  (3)

$140-148^\circ$  (4)

$53-51^\circ$  at 20 mm. (4) (5)

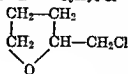
$D_4^{23} = 1.1404$  (4)  $n_D^{23} = 1.478$  (4)

$D_4^{15} = 1.1422$  (4)

$D_4^2 = 1.1500$  (4)

Colorless lachrymatory liq. gradually becoming colored in light. — Spar. sol. aq.; eas. sol. alc., ether,  $\text{CHCl}_3$ . — Volatile with steam. — Note that although two geometrical isomers are possible only this one (configuration uncertain) is known.

3:8152 TETRAHYDRO- $\alpha$ -FURFURYL CHLORIDE  $C_5H_7OCl$  Beil. S.N. 2362  
(2-(Chloromethyl)tetrahydrofuran)



B.P. 150-151° at 762 mm. (1)  $D_4^{20} = 1.1102$  (2)  $n_D^{20} = 1.4560$  (2)  
149.0-149.5° at 721 mm. (2)  
47-48° at 15 mm. (3)  $n_D^{15} = 1.45922$  (1)  
41-42° at 11 mm. (3)  
38.5-39° at 10 mm. (2)

Water-white liq. with mild and pleasant odor. —  $\bar{C}$  has no lachrymatory properties and is relatively stable (2); its chlorine atom is extremely unreactive (2).

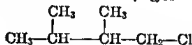
[For prepn. of  $\bar{C}$  from tetrahydro- $\alpha$ -furfuryl alcohol (1:6445) with  $\text{SOCl}_2$  + pyridine (yields: 75% (2), 73-75% (3)) see indic. refs.; note that attempts to replace  $\text{SOCl}_2$  by  $\text{PCl}_3$  (excess) in dry ether (2) were not successful; for formn. of  $\bar{C}$  from 5-chloropentenediol-1,4 (1) by dehydrative ring closure with 15%  $\text{H}_2\text{SO}_4$  at 100° for 2 hrs. (19% yield) see (1).]

$\bar{C}$  with metallic Na in dry ether under reflux, subsequently decomposed by water, gives (yields: 82% (4), 76-83% (3)) penten-4-ol-1 (penten-1-ol-5) [Beil. I-443, I<sub>2</sub>-(483)], b.p. 141.0-141.5° at 758 mm. (5), 139° at 760 mm. (6), 138.8-139.3° at 760 mm. (7);  $D_4^{25} = 0.8588$  (7),  $D_4^{20} = 0.8457$  (5);  $n_D^{20} = 1.43085$  (5),  $n_D^{15.5} = 1.4312$  (8),  $n_D^{15} = 1.4305$  (9) (corresp. allophanate, m.p. 143° (6), 147-148° (9); corresp. *N*-phenylcarbamate, oil, b.p. 183.5° at 16 mm. (8)).

$\bar{C}$  with thiourea refluxed in alc. 4 days gives (10) *S*-(tetrahydro- $\alpha$ -furfuryl)isothiouraea, isolated as corresp. picrate, m.p. 153.0-153.5° (10).

3:8152 (1) Paul, *Ann. chim.* (10) 18, 385-386 (1932). (2) Kirner, *J. Am. Chem. Soc.* 52, 3251-3255 (1930). (3) Brooks, Snyder, *Org. Syntheses* 25, 84-86 (1945). (4) Gaubert, Linstead, Rydon, *J. Chem. Soc.* 1937, 1972. (5) Juvala, *Ber.* 63, 1993 (1930). (6) Paul, *Compt. rend.* 193, 1290-1291 (1932). (7) Ginnings, Herring, Coltrane, *J. Am. Chem. Soc.* 61, 807 (1939). (8) Robinson, Smith, *J. Chem. Soc.* 1936, 196. (9) Paul, *Compt. rend.* 192, 1574 (1931). (10) Sprague, Johnson, *J. Am. Chem. Soc.* 59, 2440-2441 (1937).

3:8153 6-CHLORO-2,3-DIMETHYLPENTANE  $C_7H_{15}Cl$  Beil. S.N. 10  
(1-Chloro-3,4-dimethylpentane)



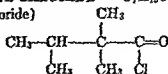
B.P. 150-151° at 745 mm. (1)  $D_4^{20} = 0.8825$  (1)  $n_D^{20} = 1.4299$  (1)  
52-53° at 20 mm. (1)

[For prepn. of  $\bar{C}$  from allyl chloride (3:7035) with 2-methylpropane (isobutane) +  $\text{AlCl}_3$  at -10° (35-40% yield accompanied by 13-15% yield 4,5-dichloro-2,2-dimethylpentane (3:8516) see (1).]

$\bar{C}$  on hydrolysis with aq.  $\text{MgO}$  in s.t. at 225° for 4 hrs. gives (54% yield (1)) 3,4-dimethylpentanol-1, b.p. 168-169°,  $n_D^{20} = 1.4288$  (corresp. 3,5-dinitrobenzoate, m.p. 51-52°; corresp. *N*-( $\alpha$ -naphthylcarbamate), m.p. 41-42°) (1).

$\bar{C}$  with Mg in dry ether gives corresp.  $\text{RMgCl}$  cpd.; this prod. on hydrolysis with aq.  $(\text{NH}_4)_2\text{SO}_4$  gives (54% yield (1)) 2,3-dimethylpentane (1:8554) or on oxidn. with air gives (62% yield (1)) 3,4-dimethylpentanol-1 (see preceding paragraph); see also below.

- 3:8145  $\alpha,\beta$ -TRIMETHYL-*n*-BUTYRYL CHLORIDE  $C_7H_{13}OCl$  Beil. S.N. 162  
(Dimethyl-isopropyl-acetyl chloride)



B.P. 148-150° {1}

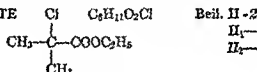
[For prepn. of  $\bar{C}$  from dimethyl-isopropyl-acetic acid [Beil. II-346, II-(147)] see {1}.]

$\bar{C}$  on hydrolysis yields dimethyl-isopropyl-acetic acid (see above), camphoraceous cryst. from pet. ether, m p. 50° {2} {3}, 41-42° {1}.

② Dimethyl-isopropyl-acet-amide: m.p. 133-134° {2}, 129° {1}.

3:8145 {1} Locquin, Leers, *Compt. rend.* 179, 55 (1924). {2} Haller, Bauer, *Compt. rend.* 149, 6 (1909). {3} Richard, *Ann. chim.* (5) 21, 353 (1910).

- 3:8147 ETHYL  $\alpha$ -CHLORO-ISOBUTYRATE  $C_6H_{11}O_2Cl$  Beil. II-295



B.P. 148.5-149° cor. {1}

148-149° {2}

147-148.5° at 760 mm. {5}

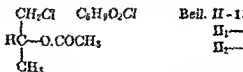
$D_4^{20} = 1.062$  {1}  $n_D^{15} = 1.4109$  {5}

[For prepn. of  $\bar{C}$  from  $\alpha$ -chloro-isobutyric acid (3:0235) with EtOH + HCl see {3}; from  $\alpha$ -chloro-isobutyryl chloride (3:5335) with EtOH see {2}.]

[ $\bar{C}$  on htg. with 1-5%  $\text{FeCl}_3$  at 100° or above loses HCl yielding {4} ethyl methacrylate, b.p. 118-119° {4}.]

3:8147 {1} Balbiano, *Ber.* 11, 1093 (1878). {2} Henry, *Rec. trav. chim.* 26, 84-85 (1907); *Compt. rend.* 142, 1023 (1906); *Bull. acad. roy. Belg.* 1906, 206-226; *Cent.* 1906, II 227. {3} Balbiano, *Gazz. chim. ital.* 8, 372 (1878). {4} Barrett (to du Pont), U.S. 2,013,648, Sept. 10, 1935; *Cent.* 1936, 1 3217; *C. A.* 29, 6902 (1935). {5} Kahovec, Kohlrausch, *Monatsh.* 74, 118 (1943).

- 3:8150  $\beta$ -CHLOROISOPROPYL ACETATE  $C_5H_9O_2Cl$  Beil. II-130  
(2-Acetoxy-1-chloropropane)



B.P. 149-150° {1} {2}

147-149° at 745 mm. {3}

$D_4^{20} = 1.0788$  {3}  $n_D^{20} = 1.4223$  {3}

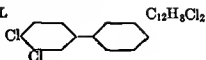
[For prepn. (72% yield {3}) from propylene + *ter*-butyl hypochlorite (3:7165) + AcOH see {3}; for prepn. from 1-chloropropanol-2 (3:7747) + AcCl see {2}; for formn. from 1,2-diacetoxypropane + HCl gas see {4}.]

1 ml aq. dis. 8 ml.  $\bar{C}$ . — With  $N/10$  HCl at 35° or 45°  $\bar{C}$  hydrolyzes much more slowly than isopropyl acetate (1.3041), but no chloride ion is liberated at 35° {1}.

⑥ 1-Phthalimido-2-acetoxypropane [Beil. XXI-(369)]. from  $\bar{C}$  on htg. 2 hrs. with K phthalimide; m.p. 99-100° {5}.

3:8150 {1} Henry, *Cent.* 1902, II 1093. {2} Bancroft, *J. Am. Chem. Soc.* 41, 427 (1919). {3} Irwin, Hennion, *J. Am. Chem. Soc.* 63, 859 (1941). {4} Dewael, *Bull. soc. chim. Belg.* 39, 400 (1930). {5} Gabriel, Ohle, *Ber.* 50, 503 (1917).

## 3:0685 2,4-DICHLOROBIPHENYL



Beil. V —  
V<sub>1</sub>—  
V<sub>2</sub>-(483)

M.P. 46° (1) B.P. 195-200° at 15 mm. (1)  
49-50° (2)

- Pale ycl. cryst. (1).

[For prepn. of  $\bar{C}$  from 3-amino-4-chlorobiphenyl (3) or from 4-amino-3-chlorobiphenyl (1) via appropriate diazo methods see (1) (3).]

$\bar{C}$  htd. with aq. alk. for 3 hrs. at 290-300° yields (4) phenylpyrocatechol (3,4-dihydroxybiphenyl) (1:1576), m.p. 144.8-145.2° (4); diacetate, m.p. 77.5-78° (4).

$\bar{C}$  on oxidn. with  $\text{CrO}_3 + \text{AcOH}$  yields (1) (3) 3,4-dichlorobenzoic acid (3:4925), m.p. 198° (3), 200° (1).

3:0685 (1) Scarborough, Waters, *J. Chem. Soc.* 1926, 500. (2) Zerweck, Schütz (to General Aniline and Film Corp.), U.S. 2,260,501, Apr. 21, 1942; *C.A.* 36, 5658 (1942). (3) Blakey, Scarborough, *J. Chem. Soc.* 1927, 3007. (4) Harvey (to E. R. Squibb and Sons), U.S. 1,952,755, March 27, 1934; *Cent.* 1934, II 1846; *C.A.* 28, 3420 (1934).

3:0700 6-CHLORO-3-METHYLPHENOL  
(2-Chloro-5-methylphenol;  
6-chloro-*m*-cresol)


 $\text{C}_7\text{H}_7\text{OCl}$ 

Beil. VI —  
VI<sub>1</sub>-(187)  
VI<sub>2</sub>-(355)

M.P. 46° (1) (3) (2) B.P. 197-198° (1)  $D_{25}^{15} = 1.215$  (5)  
45° (4) 190° at 760 mm. (5) (3)  
85° at 15 mm. (2)

Strong camphoraceous odor! — Cryst. from ice-cold lt. pet. ether (3) (2). — Volatile with steam (2).

[For prepn. from 4-chloro-3-aminotoluene (2-chloro-5-methylaniline) [Beil. XII-871] via diazo reaction see (1) (2) (4); from 6-amino-*m*-cresol (2-amino-5-methylphenol) [Beil. XIII-590] see (1).]

$\bar{C}$  treated with  $(\text{CH}_3)_2\text{SO}_4 + \text{aq. NaOH}$  gives its methyl ether, 2-chloro-5-methylanisole, b.p. 212.5° (3). [This methyl ether on oxidn. with dil.  $\text{KMnO}_4$  (2.7 hrs. for 5 g.) gave (3) 4-chloro-3-methoxybenzoic ac., pr. from 50% alc. or pl. from  $\text{CHCl}_3$ , m.p. 211° (3), Ncut. Eq. 186.5.]

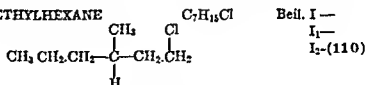
- ① 6-Chloro-3-methylphenyl benzoate: from  $\bar{C} + \text{BzCl} + \text{pyridine}$ ; pr. contg. alc. (3) from alc., m.p. 31° (3), 38° (1); cryst. from lt. pet. ether, m.p. 40° (3).
- ② 6-Chloro-3-methylphenyl benzenesulfonate: from  $\bar{C} + \text{benzenesulfonyl chloride} + \text{pyridine}$ ; cryst. from alc., m.p. 99° (1).
- ③ 6-Chloro-3-methylphenyl *p*-toluenesulfonate: from  $\bar{C} + p\text{-toluenesulfonyl chloride} + \text{pyridine}$ ; hexag. pr. from alc. (3) (1) or acetone (3), m.p. 96° (3), 93-94° (1).

3:0700 (1) Houston, Chen, *J. Am. Chem. Soc.* 55, 4214-4216 (1933). (2) Kraay, *Rec. trav. chim.* 49, 1090 (1930). (3) Gibson, *J. Chem. Soc.* 1926, 1424-1425. (4) Hodgson, Moore, *J. Chem. Soc.* 1926, 2038-2039. (5) Rascbig, *Ger.* 232,071, March 4, 1911; *Cent.* 1911, I 854.

④  $\gamma$ , $\delta$ -Dimethylcaproanilide: nacreous flakes from dil. alc., m.p. 80-81° (1). [From  $\bar{C}$  by conversion to RMgCl and reaction with phenyl isocyanate (1) according to method of (2) cf. (3).]

3:8153 (1) Schmerling, *J. Am. Chem. Soc.* 67, 1438-1441 (1945). (2) Schwartz, Johnson, *J. Am. Chem. Soc.* 53, 1063-1068 (1931). (3) Underwood, Gale, *J. Am. Chem. Soc.* 56, 2117-2120 (1934).

3:8155 *d,l*-1-CHLORO-3-METHYLHEXANE



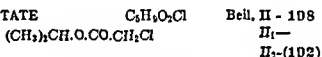
B.P. 150-152° at 768 mm. (1)

$D_4^{20} = 0.8766$  (1)  $n_D^{20} = 1.4274$  (1)

[For prepn. of  $\bar{C}$  from 3-methylhexanol-1 [Beil. I<sub>2</sub>-(445)] with alc. HCl in *s.t.* at 100° see (1).] [The dextrorotatory form of  $\bar{C}$  has also been prepd. (2) from levorotatory 3-methylhexanol-1 with  $\text{SOCl}_2$ ; b.p. 66° at 25 mm.;  $D_4^{20} = 0.854$ ;  $n_D^{30} = 1.4282$  (2).]

3:8155 (1) Dewael, Weckering, *Bull. soc. chim. Belg.* 33, 498 (1924). (2) Levene, Marker, *J. Biol. Chem.* 91, 90 (1931).

3:8160 ISOPROPYL CHLOROACETATE



B.P. 150.4-151.6° (1)

$D_4^{25} = 1.0812$  (3)  $n_D^{25} = 1.4175$  (3)

140.5° at 760 mm. (2)

$D_4^{20} = 1.0888$  (5)  $n_D^{20} = 1.4102$  (5)

140.5° at 747 mm. (3)

$D_4^{15} = 1.0944$  (4)

140-150° at 760 mm. (4)

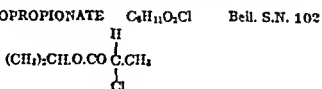
Oil with agreeable odor; insol. aq., sol. alc., ether.

[For prepn. (38.8% yield (3)) from isopropyl alc. (1:6135) + chloroacetic ac. (3:1370) see (3) (4); for prepn. (34.2% yield (3)) from propylene + chloroacetic ac. (3:1370) see (3).]

[For study of insecticidal action of vapor of  $\bar{C}$  see (2) ]

3:8160 (1) Cheng, *Z. physik. Chem.* B-24, 309 (1934). (2) Roark, Cotton, *Ind. Eng. Chem.* 20, 512-514 (1928). (3) Dorris, Sowa, Nieuwland, *J. Am. Chem. Soc.* 56, 2659-2660 (1934). (4) Steinlen, *Mull. acad. roy. Belg.* (3) 31, 101-108 (1897). *Cent.* 1897, II 659. (5) Schjanberg, *Z. physik. Chem.* A-172, 228 (1935).

3:8105 ISOPROPYL *d,l*- $\alpha$ -CHLOROPROPIONATE



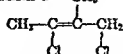
B.P. 151.5-152.5° at 760 mm. (1)

$D_4^{20} = 1.0315$  (2)  $n_D^{20} = 1.4149$  (2)

46.1-46.0° at 12 mm. (1)

3:8165 (1) Burkard, Kahovec, *Monatsh.* 71, 310 (1935). (2) Schjanberg, *Z. physik. Chem.* A-172, 230 (1935).

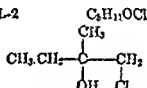


3:8170 1,3-DICHLORO-2-METHYLBUTENE-2  $\text{CH}_3$   $\text{C}_2\text{H}_3\text{Cl}_2$  Beil. S.N. 11

B.P. 151-153° (1)

 $D_4^{19} = 1.1276$  (1)  $n_D^{20} = 1.4737$  (1)Two geom. stereoisomers of  $\dot{\text{C}}$  are possible, but only this one has been reported.[For formn. of  $\dot{\text{C}}$  from 1,2,3-trichloro-2-methylbutane (3:6100) by loss of 1 HCl through distn. over KOH see (2); from 3,3-dichloro-2-methylbutene-1 (3:7690) by htg. (allylic transposition) see (1).] $\dot{\text{C}}$  on oxidn. with  $\text{KMnO}_4$  in acetone gives (2) acetic acid (1:1010) and methylglyoxal [Beil. 1-762, I<sub>1</sub>-(395), I<sub>2</sub>-(819)].3:8170 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938), *Cent.* 1939, II 4223; *C.A.* 33, 4190 (1939). (2) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 6, 1116-1132 (1936); *Cent.* 1937, 1 573, *C.A.* 31, 1003 (1937).

## 3:8175 1-CHLORO-2-METHYLBUTANOL-2

(unsym.-Ethyl-methyl-ethylene  
chlorohydrin; chloromethyl-ethyl-  
methyl-carbinol)

Beil. I - 389

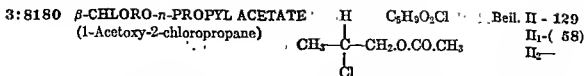
I<sub>1</sub>-(196)I<sub>2</sub>-(424)

B.P. 152-153° (1)

145-149° (2)

 $D_4^0 = 1.068$  (1)[For prepn. of  $\dot{\text{C}}$  from chloroacetone (3:5425) with  $\text{EtMgBr}$  see (1) (2) (3) (4) (5); note that in this reactn.  $\dot{\text{C}}$  is accompanied by 3-methylhexanol-4 (Beil. I-116), whose b.p. (150°) is so close to that of  $\dot{\text{C}}$  that separation by distillation is impossible.] $\dot{\text{C}}$  on distillation (5) or on treatment with  $\text{Ac}_2\text{O} + \text{conc. H}_2\text{SO}_4$  (5) yields 1-chloro-2-methylbutene-1 (3:7303) and 1-chloro-2-methylbutene-2 (3:7485);  $\dot{\text{C}}$  on distn. over anhydrous oxalic acid (1:0535) yields (6) both these halo-olefins and also 2-(chloromethyl)-butene-1 (3:9214). [ $\dot{\text{C}}$  on distn. over anhydrous oxalic acid (1:0535) and passing the resultant vapors over soda-lime or burnt lime at 600° yields (7) 2-methylbutadiene-1,3 (isoprene) (1:8020).] $\dot{\text{C}}$  with  $\text{PCl}_5$  yields (5) 1-chloro-2-methylbutene-1 (3:7303). $\dot{\text{C}}$  with conc. aq.  $\text{NaOH}$  at 40-50° gives (63% yield) (9) (1) (1) (10) 1,2-epoxy-2-methylbutane (unsym.-ethyl-methyl-ethylene oxide) [Beil. XVII-13, XVII-(8)], b.p. 82°.3:8175 (1) Fournneau, Tiffeneau, *Compt. rend.* 145, 437-438 (1907). (2) Tiffeneau, *Compt. rend.* 134, 774 (1902). (3) Bruylants, *Bull. acad. roy. Belg.* (5) 17, 1004-1026 (1931). (4) Kyriakides, *J. Am. Chem. Soc.* 36, 657-663 (1914). (5) Seyer, Chalmers, *Trans. Roy. Soc. Can.* (3) 20, 111 337 (1926); *Cent.* 1927, II 1811; *C.A.* 21, 2663 (1927). (6) Chalmers, *Trans. Roy. Soc. Can.* (3) 22, 111 75-76 (1928), *Cent.* 1929, I 632; *C.A.* 23, 2694 (1929). (7) Harries, *Ann.* 353, 178 (1911). (8) Harries, *Ger.* 243,075 + 243,076, Jan. 31, 1912; *Cent.* 1912, I 635. (9) Fournneau, Benoit, Firmenich, *Bull. soc. chim.* (4) 47, 670 (1930). (10) Riedel, *Ger.* 197,148, June 3, 1908; *Cent.* 1909, II 121.





B.P. 152-153° at 760 mm. (1)

 $D_4^{20} = 1.095$  (2);  $n_D^{20} = 1.42213$  (2)

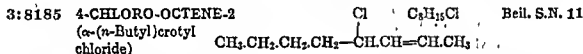
151-152° at 768 mm. (2)

 $D_{20}^{20} = 1.098$  (3)

Colorless oil with agreeable odor. — Insol aq.

[Note that  $\bar{C}$  has never been obtd. in authentically pure state. The prepn. of Henry (1) was later shown (4) to be actually a mixt. of  $\bar{C}$  with 2-acetoxy-1-chloropropane (3:8150); that of Dewael (2) was admittedly such a mixture.]

Henry's material was obtd. from 1-chloropropanol-2 by treatment with KOAc and conversion of the presumably resultant 1-acetoxypropanol-2 with  $\text{SOCl}_2$  to  $\bar{C}$ ; Dewael's material was obtd. from 1,2-diacetoxyp propane by treatment with HCl gas.

3:8180 (1) Henry, *Cent. 1902*, II 929, 1093. (2) Dewael, *Bull. soc. chim. Belg.* 39, 400 (1930).(3) Henry, *Cent. 1903*, II 486. (4) Gabriel, Ohle, *Ber.* 50, 806 (1917).

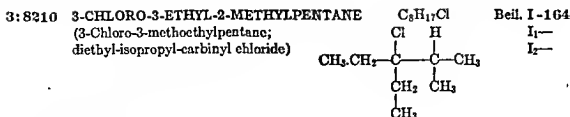
B.P. 153° (1)

 $D_4^{20} = 0.8924$  (2)  $n_D^{25} = 1.4590$  (1)

69-70° at 9 mm. (2)

0.8816 (1);  $n_D^{20} = 1.4452$  (2)

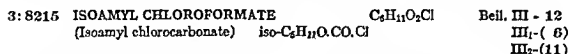
Note that two geom. stereoisomers of  $\bar{C}$  are possible; also the possibility that by allylic transposition  $\bar{C}$  may react in the form of its as yet unrecognized synionic isomer, 2-chlorooctene-3.



B.P. 150-155° dec. (1).

[For prepn. from 3-ethyl-2-methylpentanol-3 (diethyl-isopropyl-carbinol) [Beil. I-423, I<sub>2</sub>-(454)] with  $\text{PCl}_5$  see (1).]

3:8210 (1) Grigorowitsch, Pavlov, *J. Russ. Phys.-Chem. Soc.* 23, 169 (1891).



B.P. 154.3° cor. (1)

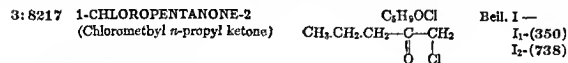
$D_4^{15} = 1.0321$  (2)  $n_{D_4^{15}} = 1.41916$  (2)

[For prepn. from isoamyl alc. (1:6200) + phosgene (3:5000) see (1).]

⑤ Isoamyl carbamate: m.p. 64.5° (3), 59° (4). [This deriv. is not recorded directly from  $\bar{C}$  but should be preparable by actn. of conc. aq.  $\text{NH}_4\text{OH}$  cf. (5).]

⑥ Isoamyl *N*-phenylcarbamate (isoamyl carbanilate): m.p. 57-58° (6), 57-59° (7), 55° (8), 55-56° (9). [This deriv. is not recorded directly from  $\bar{C}$  but should be preparable by actn. of aniline, cf. (5).]

3:8215 (1) Roese, *Ann.* 205, 230 (1890). (2) von Auwers, *Ber.* 60, 2140 (1927). (3) Marckwald, *Ber.* 37, 1040 (1904). (4) Béhal, *Bull. soc. chim.* (4) 25, 480 (1919). (5) Chattaway, Saerens, *J. Chem. Soc.* 117, 708-711 (1920). (6) Locquin, *Bull. soc. chim.* (3) 31, 600 (1904). (7) Levene, Allen, *J. Biol. Chem.* 27, 440 (1910). (8) Marckwald, *Ber.* 37, 1049 (1904). (9) Nekrasow, Melnikow, *J. prakt. Chem.* (2) 126, 02 (1930).



B.P. 154.5-156° sl. dec. (1)

58-59° at 17 mm. (1)

55-57° at 15 mm. (2)

Liquid with penetrating odor. — Very spar. sol. aq.; volatile with steam.

[For prepn. of  $\bar{C}$  from 1-chloropentanol-2 (3:8225) by oxidn. with  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$  see (2); from 2-chloromethyl-4-methyl-2-propyl-1,3-dioxolone-5 [Beil. XIX<sub>1</sub>-(657)] by hydrolytic cleavage with alk., or from 2-chloromethyl-4,4-dimethyl-2-propyl-1,3-dioxolone-5 [Beil. XIX<sub>1</sub>-(657)] by hydrolytic cleavage with aq.  $\text{HCl}/\text{AcOH}$  on warming (75-80% yield), see (1).]

[ $\bar{C}$  with dry K formate in MeOH refluxed overnight yields (2) pentanone-2-ol-1 [Beil. I<sub>2</sub>-(872)], b.p. 62-64° at 18 mm. (2), 54-56° at 11 mm.,  $D_4^{20} = 0.9860$ ,  $n_{D_4^{20}} = 1.4234$  (3).]

$\bar{C}$  readily forms a cpd. with satd. aq.  $\text{NaHSO}_3$  soln. (2).

$\bar{C}$  does not react (4) with benzenediazonium hydroxide (diazotized aniline in  $\text{NaOAc}$  soln.), cf. chloroacetone (3:5425).

⑩ 1-Chloropentanon-2 semicarbazone: m.p. 157° (instantaneous fusion on Hg bath) with decomp. (1).

3:8217 (1) Blaise, *Bull. soc. chim.* (4) 15, 672-673 (1914); *Compt. rend.* 155, 48 (1912). (2) Levene, Haller, *J. Biol. Chem.* 77, 560-561 (1928). (3) Schmidt, Ascherl, *Ber.* 58, 358 (1925). (4) Favrel, *Bull. soc. chim.* (5) 1, 990 (1934).

3:8219 1-CHLOROHEPTENE-1  $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCl}$   $\text{C}_7\text{H}_{13}\text{Cl}$  Beil. I - 219

I<sub>1</sub>—  
I<sub>2</sub>-(196)

B.P. 155° cor. (1)

149-150° at 733 mm. (2)

148° (3)

78-82° at 75 mm. (4)

Note that although two geom. stereoisomers of  $\bar{\text{C}}$  are possible only one has yet been recognized.

[For prepn. of  $\bar{\text{C}}$  from 1,1-dichloroheptane (3:8650) by elimination of 1 HCl with alc. KOH (1) (3) (note, however, that yields are low (4) and the process has sometimes (5) failed), or better large excess solid KOH at 200° (62% yield (4)), see indic. refs.; from *n*-heptaldehyde (1:0183) with  $\text{PCl}_5$  see (6).]

$\bar{\text{C}}$  with KOH in mineral oil at 250° (4), or with  $\text{NaNH}_2$  in toluene or xylene at 100-150° (6), or in mineral oil (Nujol) at 150-155° (7) gives (yields: 54% (7), 37% (4)) heptyne-1 (1:8085), b.p. 98°.

[ $\bar{\text{C}}$  with perbenzoic acid (benzoyl hydrogen peroxide) in  $\text{CHCl}_3$  for 25 days gives (2) corresp. oxide, viz., 1-chloro-1,2-epoxyheptane, b.p. 93-95° at 50 mm.,  $D_4^{20} = 0.9874$ ,  $n_D^{20} = 1.4370$  (2).]

[ $\bar{\text{C}}$  with  $\text{NaSC}_2\text{H}_5$  in *n*-BuOH under reflux or better in EtOH at 138° under pressure gives (8) ethyl hepten-1-yl sulfide, b.p. 196-202°.]

3:8219 (1) Limpicht, *Ann.* 177, 33-34 (1872). (2) Guest, *Chem. Soc. Trans.* 1924, 1098 (1924). (3) Welt, *Ber.* 30, 1496 (1897).

*J. Am. Chem. Soc.* 47, 801 (1925).

(7) Johnson, McEwen, *J. Am. Chem. Soc.* 48, 473 (1926). (8) Loevenich, Losen, Dierichs, *Ber.* 60, 954 (1927).

3:8220 *ter*-BUTYL CHLOROACETATE  $\text{C}_6\text{H}_{11}\text{O}_2\text{Cl}$  Beil. S.N. 160  
( $\text{CH}_3$ )<sub>3</sub>C.O.CO.CH<sub>2</sub>Cl

B.P. 155° sl. dec. (1)

60.2° at 15 mm. (1)

48-49° at 11 mm. (2)

$n_D^{20} = 1.4260$  (2)

1.4230 (1)

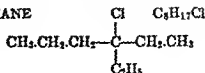
Colorless liq. heavier than aq. (1).

[For prepn. (yield: 63% (2), 60% (1)) from *ter*-butyl alc. (1:6140) + chloroacetyl chloride (3:5235) + dimethylaniline see (1) (2).]

Hydrolysis yields (1) *ter*-butyl alc. (1:6140) + chloroacetic acid (3:1370) (1); Sap. Eq. = 150.5 (1).

3:8220 (1) Westheimer, Shookhoff, *J. Am. Chem. Soc.* 62, 271 (1940). (2) Baker, *Org. Syntheses* 24, 21 (1944).

3:8223 3-CHLORO-3-ETHYLHEXANE  
(Diethyl-*n*-propyl-carbinyl  
chloride)



Beil. I - 162  
I<sub>1</sub>—  
I<sub>2</sub>-(126)

B.P. 155° sl. dec. (1)

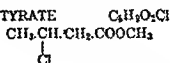
[For prepn. of  $\bar{C}$  from 3-ethylhexanol-3 (diethyl-*n*-propyl-carbinol) [Beil. I-421, I<sub>1</sub>-(210), I<sub>2</sub>-(454)] with  $\text{PCl}_5$  see (1).]

[ $\bar{C}$  with diethylamine loses  $\text{HCl}$  (2) yielding an olefin (2).]

[For data on density and parachor of  $\bar{C}$  at 0°, 15°, 25°, 50°, and 65° see (3).]

3:8223 (1) Butlerow, *Bull. soc. chim.* (2) 5, 23 (1866). (2) Montagne, *Ann. chim.* (10) 13, 111 (1930). (3) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* 61, 3107-3111 (1939).

3:8224 METHYL *d,l*- $\beta$ -CHLORO-*n*-BUTYRATE



Beil. II - 277  
II<sub>1</sub>—  
II<sub>2</sub>—

B.P. 155-156° at 760 mm. (1)

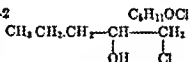
$D_4^{20} = 1.0996$  (2)  $n_D^{20} = 1.4258$  (2)

[For prepn. of  $\bar{C}$  from methyl crotonate (1:3121) by addn. of  $\text{HCl}$ , from  $\beta$ -chloro-*n*-butyronitrile +  $\text{MeOH}$  +  $\text{HCl}$ , or from methyl *n*-butyrate (1:3080) with  $\text{Cl}_2$  see (1).]

$\bar{C}$  on hydrolysis yields  $\text{MeOH}$  (1:6120), crotonic acid (1.0425), and  $\text{HCl}$ .

3:8224 (1) Henry, *Bull. acad. roy. Belg.* (3) 35, 607-620 (1893); *Cent.* 1893, II 273. (2) Schjaneberg, *Z. physik. Chem.* A-172, 232 (1935).

3:8225 *d,l*-1-CHLOROPENTANOL-2  
(Chloromethyl-*n*-propyl-  
carbinol; *n*-propylethylene  
chlorohydrin)



Beil. I —  
I<sub>1</sub>—  
I<sub>2</sub>-(419)

B.P. 157-160° at 735 mm. (1)

$D_{20}^{25} = 1.0143$  (1)  $n_D^{25} = 1.4404$  (1)

68-75° at 30 mm. (2)

$D_{20}^{20} = 1.037$  (2)  $n_D^{20} = 1.4520$  (2)

66-67° at 18 mm. (3)

1.031 (3) 1.4422 (3)

59-62° at 14 mm. (4)

[For prepn. of  $\bar{C}$  from pentene-1 (1:8205) with  $\text{HOCl}$  (43% yield) see (2); from 1-chloro-2,3-epoxypropane (epichlorohydrin) (3:5358) with  $\text{MgEt}_2$  (70% yield (3)) or with  $\text{EtMgBr}$  (16-10% yield (1)) see indic. refs.; from chloroacetaldehyde (3:7212) with *n*- $\text{PrMgBr}$  see (4).]

$\bar{C}$  with  $\text{AcCl}$  yields (1) 1-chloro-2-acetoxypentane, b.p. 186-188° at 740 mm.,  $D_{20}^{25} = 1.0825$ ,  $n_D^{25} = 1.4328$  (1);  $\bar{C}$  with  $\text{NaSMc}$  gives (45% yield (2)) 1-methylthiopentanol-2, b.p. 90° at 18 mm.,  $D_{20}^{20} = 0.913$ ,  $n_D^{20} = 1.4792$  (2);  $\bar{C}$  with  $\text{SOCl}_2$  + diethylaniline gives (70% yield (1)) 1,2-dichloropentane (3:8140);  $\bar{C}$  with 2 moles  $\text{EtMgBr}$  yields (3) heptanol-4 (1:6228).

$\bar{C}$  on oxidn. with  $\text{K}_2\text{Cr}_2\text{O}_7$  +  $\text{H}_2\text{SO}_4$  yields (4) 1-chloropentanone-2 (3:8217), b.p. 55-57° at 15 mm (4);  $\bar{C}$  on oxidn. with aq.  $\text{KMnO}_4$  yields (1) *n*-butyric acid (1:1035) q.v.

⊙ Chloromethyl-*n*-propyl-carbinyl 3,5-dinitrobenzoate: pl. from alc., m.p. 84-85° (3), 83-84° (1), from  $\bar{C}$  on litg. with 3,5-dinitrobenzoyl chloride until no more  $\text{HCl}$  is evolved (1).

3:8225 (1) Koelsch, McElvain, *J. Am. Chem. Soc.* **51**, 3392, 3393 (1929). (2) Glavis, Ryden, Marvel, *J. Am. Chem. Soc.* **59**, 709 (1937). (3) Magrane, Cottle, *J. Am. Chem. Soc.* **64**, 484-487 (1942). (4) Levene, Haller, *J. Biol. Chem.* **77**, 560 (1928).

3:8228 CHLOROACETALDEHYDE DIETHYLACETAL  $C_6H_{13}O_2Cl$  Beil. I - 611  
(Chloroacetal)  $CH_2-CH(OC_2H_5)_2$  I<sub>1</sub>-(328)  
 $Cl$  I<sub>2</sub>-(676)  
B.P. 157.4° (1)  
157-158° (11)  $D_{20}^{20} = 1.017$  (3)  $n_D^{20} = 1.4171$  (3)  
156.8° cor. at 756.8 mm. (2)  
156° (13)  
53-54° at 16 mm. (3)

[For prepn. from vinyl acetate (b.p. 69-71°) by treatment in abs. EtOH soln. with  $Cl_2$  in dark and in a solid  $CO_2$ /acetone cooling bath (83% yield) see (3); from acetaldehyde diethylacetal ("acetal") (1:0156) with  $Cl_2$  at 50° in presence of abs. alc. NaOEt (90% yield) see (4); from paraldehyde (1:0170) by chlorination and subsequent treatment with EtOH see (5) (6); from EtOH (1:6130) by treatment with  $Cl_2$  see (7) (8).]

[For prepn. of  $\bar{C}$  from chloroacetaldehyde (3:7212) on warming with EtOH see (9); from chloroacetaldehyde ethyl alcoholate (chloroacetaldehyde ethyl-hemi-acetal) [Beil. I-611] in EtOH with dry HCl gas see (10); from  $\alpha,\beta$ -dichloroethyl ethyl ether (3:5640) with 2 vols. abs. EtOH (2) or with NaOEt (11) (12) (13) see indic. refs.]

$\bar{C}$  is comm. chem. in U.S. (1943) (14);  $\bar{C}$  is widely used in org. synthesis as source of combined chloroacetaldehyde (3:7212) and otherwise.

The acetal portion of  $\bar{C}$  is stable to alkali but readily hydrolyzed by aq. acids; the chlorine atom, however, behaves like a reactive alkyl halide; all these characteristics are illustrated in the reactns. cited below.

$\bar{C}$  on warming with dil.  $H_2SO_4$  yields (15) chloroacetaldehyde (3:7212) accompanied by some *bis*-( $\beta$ -chloro- $\alpha$ -ethoxyethyl) ether, h.p. aht. 165°;  $\bar{C}$  on satn. at 100° with dry HCl gas yields (9)  $\alpha,\beta$ -dichloroethyl ethyl ether (3:5640). —  $\bar{C}$  on htg. with AcOH at 120° or with anhydrous oxalic acid at 100-150° yields (12) chloroacetaldehyde (3:7212) + ethyl acetate (1:3015) or diethyl oxalate (1:1055) respectively.

[ $\bar{C}$  htd. with NaOEt in s.t. at 140-150° for 30 hrs. (11) (13) (17) or with abs. alc. NaOEt at 160° under press. (16) gives (66% yield (16)) ethoxyacetaldehyde diethylacetal, b.p. 168° (11) (this prod. on htlg. with dil.  $H_2SO_4$  (17) (13) (16) hydrolyzes to EtOH (1:6130) + ethoxyacetaldehyde (1:0159), h.p. 105-106°). —  $\bar{C}$  htd. with 10% excess of satd. abs. alc. KOH in s.t. for 75 hrs. gives (95% yield (18)) glycolaldehyde diethylacetal (hydroxyacetaldehyde diethylacetal) (1:0191), b.p. 167°.] [For reactn. of  $\bar{C}$  with many other alcs. (19) (20) and phenols (21) in pres. of alk. see indic. refs.]

[ $\bar{C}$  htd. with Na or Mg at 120-130° (22) or with Na in ether at 0-20° (23) yields ethyl

[ $\bar{C}$  htd. with 4-5 vols. conc. aq.  $NH_4OH$  in s.t. at 130° for 12-14 hrs. (25) or  $\bar{C}$  in satd. alc.  $NH_3$  in s.t. at 130° (26) (27) (28) or refluxed in pres. of NaI (29) yields aminoacetaldehyde diethylacetal [Beil. IV-308, IV<sub>1</sub>-(449), IV<sub>2</sub>-(758)], b.p. 163°. —  $\bar{C}$  htd. with alc. hydrazine hydrate under press. for 6 hrs. at 115-120° yields (30) hydrazinoacetaldehyde diethylacetal [Beil. IV-553].]

[ $\bar{C}$  with aniline +  $NaNH_2$  in ether gives (77% yield (31)) *N*-(phenyl)aminoacetalde-

hyde diethylacetal [Beil. XII-213], b.p. 92-94° at 0.3 mm.; for corresp. behavior with benzylamine (32) or primary alph. amines (33) see indic. refs.] —  $\bar{C}$  with 3 moles phenylhydrazine htd. several hrs. at 130° yields (34) glyoxal-bis-(phenylhydrazone), yel. tbls. from alc. or ether, m.p. 177° u.e., 179° cor. (34).

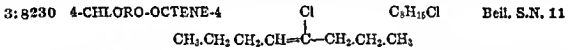
$\bar{C}$  on acid hydrolysis (3) yields ethyl alcohol (1:6130) and chloroacetaldehyde (3:7212) q.v.

3:8228 (1) Lecat, *Rec. trav. chim.* 45, 622 (1926). (2) Paterno, Mazzara, *Gazz. chim. ital.* 3, 254-256 (1873), *Ber.* 6, 1202 (1873). (3) Filachione, *J. Am. Chem. Soc.* 61, 1705-1706 (1939). (4) Anselm, Calitzstein, *Ger.* 639,507, Dec. 7, 1936; *Cent.* 1937, 1 2023; *C.A.* 31, 3940 (1927). (5) Freundler, *Bull. soc. chim.* (4) 1, 70-71 (1907). (6) Soc. des Usines Chimiques Rhone-Poulenc, French 711,095, Sept. 2, 1931; *Cent.* 1932, 1 130. (7) Lieben, *Ann.* 104, 114-115 (1857). (8) Fritsch, *Ann.* 279, 300 (1879). (9) Natterer, *Monatsh.* 5, 497-499 (1884). (10) Fritsch, Schumacher, *Ann.* 279, 308 (1894).

(11) Lieben, *Ann.* 146, 193-201 (1868). (12) Natterer, *Monatsh.* 3, 444-449 (1882). (13) Kluger, *Monatsh.* 26, 880-882 (1905). (14) *Chem. Ber.* 71, 1888 (1898). (15) Sabetay, *Bull. soc. chim.* (4) 1, 129-136 (1933); *Cent.* 1933, II 2694. (21) Parfumerie Houbigant, Sabetay, French 673,379, Feb. 14, 1930; *Cent.* 1930, II 2694.

(22) Wislicenus, *Ann.* 192, 106-109 (1878). (23) Leuchs, Lemcke, *Ber.* 47, 2577 (1914). (24) Späth, *Monatsh.* 35, 466-467 (1914). (25) Wolff, *Ber.* 21, 1482 (1888); 26, 1832 (1893). (26) Wolff, Marburg, *Ann.* 363, 179-182 (1908). (27) Marckwald, *Ber.* 25, 2355 (1892). (28) Buck, Wrenn, *J. Am. Chem. Soc.* 51, 3613 (1929). (29) Wohl, *Ber.* 39, 1953 (1906). (30) Fischer, Hunsalz, *Ber.* 27, 178-179 (1894).

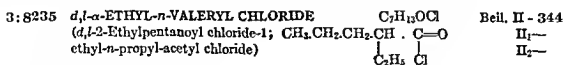
(31) Wohl, Lange, *Ber.* 40, 4728 (1907). (32) Rügheimer, Schön, *Ber.* 41, 17-18 (1908). (33) Paal, van Gemmer, *Arch. Pharm.* 246, 306-314 (1908). (34) Fischer, *Ber.* 26, 97 (1893).



B.P. 157-159.5° at 760 mm. (1)  $D_4^{25} = 0.8788$  (1)  $n_D^{25} = 1.4394$  (1)

Although two geom. stereoisomers of  $\bar{C}$  are possible only this one has as yet been reported. [For prepn. of  $\bar{C}$  from octyne-4 (di-*n*-propylacetylene) (1:8110) with  $\text{AcCl} + \text{SnCl}_4$  (both stereoisomers of 4-chloro-3-*n*-propylhepten-3-one-2 are also formed: *cis*, b.p. 117-118° at 28 mm.,  $D_4^{25} = 0.9680$ ,  $n_D^{25} = 1.4587$ ; *trans*, b.p. 112-113° at 23 mm.,  $D_4^{25} = 0.9592$ ,  $n_D^{25} = 1.4601$  (1)) see (1).]

3:8230 (1) Kroeger, Sowa, Nieuwland, *J. Org. Chem.* 1, 163-169 (1936).



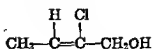
B.P. 158-160° (1)  
50° at 11 mm. (2)

[For prepn. of  $\bar{C}$  from 2-ethylpentanoic acid-1 (ethyl-*n*-propyl-acetic acid) (1:1133) with  $\text{PCl}_3$  (1) or  $\text{SOCl}_2$  (2) see indic. refs.]

$\bar{C}$  on hydrolysis yields ethyl-*n*-propyl-acetic acid (1:1133) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to  $\bar{C}$  see 1:1133).

3:8235 (1) Rasetti, *Bull. soc. chim.* (3) 33, 687 (1905). (2) Reichstein, Trivelli, *Helv. Chim. Acta* 16, 974 (1933); 15, 258-259 (1932).

**3:8240 2-CHLOROBUTEN-2-OL-1**  
( $\beta$ -Chlorocrotonyl alcohol)



$\text{C}_4\text{H}_7\text{OCl}$  Beil. I - 442  
 $I_1-$   
 $I_2-(481)$

B.P. 159° at 760 mm. (1)  
158-161° (2)  
158.3° cor. at 742.5 mm. (3)  
52-53° at 19 mm. (4)

$D_4^{23} = 1.0950$  (4)  $n_D^{23} = 1.45093$  (4)  
 $D_4^{20} = 1.118$  (1)  $n_D^{20} = 1.46823$  (1)

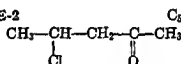
Note: *cis* and *trans* stereoisomers of  $\tilde{\text{C}}$  are theoretically possible but have not definitely been reported.

[For prepn. of  $\tilde{\text{C}}$  from 2-chlorobuten-2-al-1 ( $\alpha$ -chlorocrotonaldehyde) (3:8117) by reduction in abs. alc. with  $\text{H}_2$  +  $\text{Al}(\text{OEt})_3$  (2) or with  $\text{Mg}(\text{OEt})_2 \cdot \text{EtOMgCl}$  (1) see (2) (1); for formn. of  $\tilde{\text{C}}$  (together with 3-chlorobuten-3-ol-2) (3:9115) from either the low-boilg (3:5360) or high-boilg. (3:5615) atereoisomer of 1,2-dichlorobutene-2 by hydrolysis with 2 pts. aq. + 1 mole  $\text{CaCO}_3$  for 4 hrs. at 70° see (4); for prepn. of  $\tilde{\text{C}}$  from 2,2,3-trichlorobutanol-1 (3:1336) with Zn dust +  $\text{HCl}$  see (3).]

② 2-Chlorobuten-2-yl-1 *N*-( $\alpha$ -naphthyl)carbamate: m.p. 95-96° (4).

3:8240 (1) Meerwein et al., *J. prakt. Chem.* (2) 147, 225 (1936). (2) I. G. Farbenindustrie, Ger. 437,160, Nov. 18, 1926; *Cent.* 1927, I 802. (3) Garzarolli-Thurnlackh, *Ann.* 213, 375-379 (1882). (4) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 7, 658-662 (1937); *Cent.* 1937, II 371-372; *C.A.* 31, 5754 (1937).

**3:8243 4-CHLOROPENTANONE-2**  
( $\beta$ -Chloro-*n*-propyl  
methyl ketone)



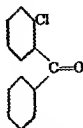
$\text{C}_5\text{H}_9\text{OCl}$  Beil. I - 678  
 $I_1-$   
 $I_2-$

B.P. 159-160° (1)

[For preparation of  $\tilde{\text{C}}$  from acetyl chloride (3:7065) + propylene in pres. of  $\text{ZnCl}_2$  see (1); for reactn. of acetyl chloride with propylene in pres. of activated carbon at 100-300° and at press of 20-200 atm. cf. (2).]

3:8243 (1) Kondakow, *J. Russ. Phys.-Chem. Soc.*, 26, 15 (1883). (2) Frohlich, Wierzevich (to Standard Oil Development Co.), U.S. 2,006,193, June 25, 1935; *Cent.* 1936, I 2827.

**3:0715 2-CHLOROBENZOPHENONE**  
(*o*-Chlorophenyl phenyl  
ketone)



$C_{13}H_9OCl$  Beil. VII - 419  
VII- (227)

M.P. 46° (1)  
45.5-46° (2)  
45.5° (3) (4) (5)  
(6) (8) (10)  
52-56° (7)

B.P. 330° (3) cor. (4)  
185-188° at 13 mm. (7)

TbIs. from  $CHCl_3$  + lgr. (3) (4); cryst. from pct. eth. (5). — [For crystallog. data see (5) (8).]

[For prepn. (93% yield (9)) from *o*-chlorobenzoyl chloride (3:0640) +  $C_6H_6$  +  $AlCl_3$  see (3) (5) (9); for formation (12%) in reaction of  $BzOH$  + chlorobenzene +  $AlCl_3$  (main prod. 4-chlorobenzophenone (3:1914)) see (2) ]

$\bar{C}$  on reduction with 10%  $Na/Hg$  + alc. (11) or boilg. alc.  $KOH$  (12) gives almost exclusively 2-chlorodiphenylcarbinol [Beil. VI-680], m.p. 65° (11) (12), 62° (19). —  $\bar{C}$  with  $Al/Hg$  + 80% alc. (6) gives mainly 2-chlorodiphenylcarbinol (above) + a little 2,2'-dichlorobenzpinacol. —  $\bar{C}$  with  $Zn$  +  $AcOH$  (11) or  $\bar{C}$  in alc. on long exposure to sunlight (11) (13) (14) gives 2,2'-dichlorobenzpinacol [Beil. VI-523], m.p. 174-175° (6), 178° dec. (11).

$\bar{C}$  htd. with aniline 3-4 hrs. at 200° yields (4) 2-chlorobenzophenone anil [Beil. XII-201], pale yel. ndls. or scales from alc., m.p. 128° (4). [Fused subst. or solns. in org. solvents (especially  $CHCl_3$ ) are yellow.]

$\bar{C}$  fused for 3 hrs. at 200° with a mixt. of  $KOH$  +  $NaOH$  gives (1)  $BzOH$  (1:0715) (90-95% yield) + chlorobenzene (3:7903) but no *o*-chlorobenzoic acid; however,  $\bar{C}$  with aq.  $NaOH$  + trace  $CaO$  in iron bomb (or in pres. of  $Fe$  powder) at 240° for 6 hrs. gives (58% yield (20)) fluorenone (1:0014).

$\bar{C}$  with  $CH_3MgI$  yields (15) 1-(*o*-chlorophenyl)-1-phenylethylene, oil, b.p. 162-163° at 18 mm. (15);  $\bar{C}$  with  $Mg$  +  $MgI_2$  easily loses nuclear halogen (16).

⑤ 2-Chlorobenzophenone oxime: from  $\bar{C}$  +  $NH_2OH \cdot HCl$  + dil. alc.  $KOH$  (5) (17) (7) or from  $\bar{C}$  +  $NH_2OH \cdot HCl$  + alc. htd. in s.t. for 3 hrs. at 130° (17); cryst. from pct. ether, m.p. 133-134° (17), 121° (5) (7). [With  $PCl_5$  in dry ether, followed by aq. this oxime yields by Beckmann rearr. *o*-chlorobenzanilide [Beil. XII-266], m.p. 118° (5), 114° (17).] [The above oxime boiled with cone. aq.  $KOH$  for 1 day (5) or refluxed 6 hrs. with 20 pts. 30%  $MeOH/KOH$ , then diluted with aq. (17) (18), gives 3-phenylindoxazene [Beil. XXVII-71], ndls. or tbIs. from ether or alc., m.p. 83-84° (18), 82.5° (5) (11).]

3:0715 (1) Lock, Rüdiger, *Ber.* 72, 867 (1939). (2) Newton, Groggins, *Ind. Eng. Chem.* 27, 1394 (1935). (3) Overton, *Ber.* 26, 28-29 (1893). (4) Graebe, Keller, *Ber.* 32, 1687 (1899). (5) Montagne, Koopal, *Rec. trav. chim.* 29, 139-145 (1910). (6) Cohen, Böeseken, *Rec. trav. chim.* 38, 114-115 (1919). (7) von Auer, Lechner, Hundemann, *Ber.* 58, 50 (1925). (8) Jaeger, *Z. Krist.* 56, 45 (1916). (9) Mayer, Freund, *Ber.* 53, 2031-2032 (1922). (10) Koopal, *Rec. trav. chim.* 31, 153 (1915).

(11) Ref. 10, pp. 157-160. (12) Montagne, van Charante, *Rec. trav. chim.* 31, 311-312 (1912). (13) Cohen, Böeseken, *Rec. trav. chim.* 39, 255 (1920). (14) Böeseken, Cohen, Langleyk, *Rec. trav. chim.* 46, 353-396 (1927). (15) Bergmann, Bondi, *Ber.* 61, 1473-1474 (1931). (16) Gom-



accompanying *p*-isomer (3:8287) varies widely, e.g., from 100%  $\bar{C}$  with  $\text{PhCl}_2 + \text{NH}_4\text{OH}$  (42), through 62% *o*/28% *p* with  $\text{PbCl}_2$  (8), to 2.5 *o*/1 *p* via the electrolytic methods (40) (for details the orig. refs. must be consulted).] — [For sepn. of  $\bar{C}$  from polychlorotoluenes via const.-boilg. mixt. with aq. see (79).]

[For prepn. of  $\bar{C}$  from hydrazone of *o*-chlorobenzaldehyde (3:6410) by Wolff-Kishner reduction (35–82% yield) see (113).]

[For thermal anal. of system:  $\bar{C} + \text{SbCl}_3$  see (48).]

[ $\bar{C}$  with  $\text{H}_2$  in pres. of  $\text{Pd}/\text{CaCO}_3$  in alc./alk. soln. loses all its chlorine as  $\text{HCl}$  (49);  $\bar{C}$  with  $\text{HI} + \text{P}$  at  $302^\circ$  for 5 hrs. gives 80% yield (50) toluene (1:7405).]

$\bar{C}$  on oxidn. with  $\text{CrO}_3$  is completely destroyed (30);  $\bar{C}$  on oxidn. with boilg. aq.  $\text{KMnO}_4$  (74–78% yield (51)) (52) (36) (53) or  $\bar{C}$  on cat. oxidn. with air over granular tin vanadate at  $287^\circ$  (13.8% yield (54)) cf. (55) or  $\bar{C} + \text{KCN} + \text{NiCl}_2$  in dil. alc. 20 hrs. at  $260\text{--}270^\circ$  (7.5% yield (63)) gives *o*-chlorobenzoic acid (3:4150);  $\bar{C}$  with  $\text{CrO}_2\text{Cl}_2$  followed by aq. (51.5% yield (56)) (57) or  $\bar{C}$  on oxidn. with Ce cpds. (58) or with air over  $\text{Ta}_2\text{O}_5$  (59) cf. (60) or  $\bar{C}$  with  $\text{MnO}_2 + \text{H}_2\text{SO}_4$  (61) or  $\text{PhO}_2 + \text{dil. H}_2\text{SO}_4$  (24% yield (62)) gives *o*-chlorobenzaldehyde (3:6410).

[ $\bar{C}$  with  $\text{Cl}_2$  in pres. of  $\text{Al}/\text{Hg}$  gives (64) a mixt. contg. 2,3- (3:6345), 2,4- (3:6290), 2,6- (3:6270), together with some 2,5-dichlorotoluene (3:6245). —  $\bar{C}$  with  $\text{Cl}_2 + 3\% \text{PCl}_5$  in light gives (65) (19) *o*-chlorobenzyl chloride (3:6400);  $\bar{C}$  with  $\text{Cl}_2 + \text{PCl}_5$  at  $150\text{--}180^\circ$  (66) (67) (68) cf. (70) gives *o*-chlorobenzal (di)chloride (3:6625);  $\bar{C}$  with  $\text{Cl}_2 + \text{PCl}_5$  (73) or with  $\text{Cl}_2$  at  $160\text{--}190^\circ$  (69) gives (64% yield (69)) (70) (71) *o*-chlorobenzotrichloride (3:6880).]

[ $\bar{C}$  with  $\text{Br}_2$  in pres. of  $\text{Al}/\text{Hg}$  in  $\text{CCl}_4$  gives (74) mainly 5-bromo-2-chlorotoluene [Beil. V-307,  $V_1$ -(165)], together with a smaller amt. of 4-bromo-2-chlorotoluene [Beil. V-307,  $V_1$ -(155)]; the former is also obtd. (75) from  $\bar{C} + \text{Br}_2 + \text{HNO}_3 + \text{H}_2\text{SO}_4$  in  $\text{AcOH}$ . —  $\bar{C}$  with  $\text{Br}_2$  (76) (77) yields *o*-chlorobenzyl bromide [Beil.  $V_1$ -(155)] (for studies of rate of side-chain bromination of  $\bar{C}$  see (78)).]

[ $\bar{C} + \text{I}_2 + \text{HNO}_3 + \text{H}_2\text{SO}_4$  in  $\text{AcOH}$  gives (75) 2-chloro-5-iodotoluene [Beil. V-315]]

[ $\bar{C}$  with  $\text{AlCl}_3 + \text{HCl}$  gas as directed (7) undergoes partial rearr. to both *m*-chlorotoluene (3:8275) and *p*-chlorotoluene (3:8287); for anal. of mixts. of the three isomers see (7).]

[ $\bar{C}$  with  $\text{AcCl}$  (80) or better  $\text{Ac}_2\text{O}$  (81) +  $\text{AlCl}_3$  gives (70% yield (81)) 4-chloro-3-methylacetophenone [Beil. VII-307], b.p.  $254.2\text{--}254.4^\circ$  at 753.4 mm.,  $n_D^{25} = 1.5521$  (81). —  $\bar{C}$  with  $\beta$ -chloropropionyl chloride (3:5690) +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives (68% yield (82)) (83) 2-chloro-5-( $\beta$ -chloropropionyl)toluene, colorless pr. from  $\text{C}_6\text{H}_6$ , m.p.  $46^\circ$  (82), which on ring closure with conc.  $\text{H}_2\text{SO}_4$  gives (82) (83) 6-chloro-7 (or 5)-methylindanone-1, cryst. from alc., m.p.  $74\text{--}75^\circ$  (82) (83). —  $\bar{C}$  with trichloroacetonitrile +  $\text{AlCl}_3$  (4 moles) at  $80\text{--}90^\circ$  satd. with  $\text{HCl}$  gas for 2 days gives (40% yield (84)) 4-chloro-3-methyl- $\alpha,\omega,\omega$ -trichloroacetophenone, b.p.  $155\text{--}160^\circ$  at 11 mm. (84). —  $\bar{C}$  with fumaryl (di)chloride +  $\text{AlCl}_3$  in  $\text{CS}_2$  at  $50\text{--}60^\circ$  for 2 hrs. gives (51% yield (85)) *trans*-bis-1,2-(4-chloro-3-methylbenzoyl)ethylene, pale yel. cryst. from alc., m.p.  $167^\circ$  (85).]

[ $\bar{C}$  with benzoyl chloride +  $\text{AlCl}_3$  gives (83% yield (86)) 3-chloro-4-methylbenzophenone [Beil. VII-(236)], lfts. from alc., m.p.  $82\text{--}83^\circ$  (86);  $\bar{C}$  with *o*-chlorobenzoyl chloride (3:6640) +  $\text{AlCl}_3$  in  $\text{CS}_2$  for 12 hrs. gives (87) 2',3'-dichloro-4-methylbenzophenone, cryst. from alc., m.p.  $43.5^\circ$  (87). —  $\bar{C}$  with naphthalene-bis-1,4 (or 5)-(dicarboxylic acid dichloride) +  $\text{AlCl}_3$  gives (88) bis-1,4 (or 5)-(chlorotoluoyn)naphthalene (used for ring closure to corresp. dihenzpyrenequinones).]

[ $\bar{C}$  with phthalic anhydride +  $\text{AlCl}_3$  at  $90^\circ$  gives (89) (90) (91) a mixt. (93% yield (90)) of two *o*-(chlorotoluoyn)benzoic acids A + B: A, m.p.  $183\text{--}184^\circ$  (90),  $182\text{--}183^\circ$  (91) (89), the main prod., is regarded variously as either (90) *o*-(3-chloro-4-methylbenzoyl)benzoic acid or (91) *o*-(4-chloro-3-methylbenzoyl)benzoic acid but in any case with conc.  $\text{H}_2\text{SO}_4$

## 3:8245 o-CHLOROTOLUENE

 $C_7H_7Cl$ 

Beil. V - 290

V<sub>1</sub>-(149)V<sub>2</sub>-(224)

## B.P.

159.45-159.55°	at 760 mm.	(1)
159.5° cor.	at 759.5 mm.	(2)
150.38°	at 760.1 mm.	(3)
159.15°	at 760 mm.	(4)
159.0-159.2° cor.		(5)
158.93-158.97°	at 760 mm.	(6)
158.7-158.9°	at 754 mm.	(7)
158.4-158.7°	at 760.4 mm.	(8)
158.3-159.3°		(9)
157.2°	at 760 mm.	(10)
147.7°	at 558.9 mm.	(3)
142.3°	at 485.0 mm.	(3)
134.2°	at 391.1 mm.	(3)
123.3°	at 279.4 mm.	(3)
112.1°	at 191.0 mm.	(3)
95.2°	at 106.0 mm.	(3)
93.2°	at 98.0 mm.	(3)
41°	at 11 mm.	(11)

## F.P.

-34.0°	(12)	$D_4^{25} = 1.07762$	(4)
-34.5°	(11)	$n_D^{25} = 1.52221$	(1)
-34.7°	(13)	$D_4^{20} = 1.08246$	(4)
-35.1°	(8)	1.08173	(14)
-36.5°	(4)	1.0785	(1)
	(10)	$n_D^{20} = 1.52691$	(4)
		$D_4^{15} = 1.08729$	(4)

[See also *p*-chlorotoluene (3:8287)]

[For f.p./compn. data on system.  $\bar{C}$  + *p*-chlorotoluene (3:8287) (eutectic, f.p. -50° conts. 73%  $\bar{C}$ ) see (8) (112); for  $D_4^{20}$ /compn. data on this system see (8); for  $n_D^{20}$ /compn. data on this system see (15). — For f.p./compn. data on systems  $\bar{C}$  + chlorobenzene (3:7903) (13),  $\bar{C}$  + *m*-dichlorobenzene (3:5960) (16),  $\bar{C}$  + bromobenzene (16) see indie. refs.]

[For prepn. of  $\bar{C}$  from *o*-toluidine [Beil. XII-772, XII<sub>1</sub>-(372)] via diazotization and use of  $Cu_2Cl_2$  reactn. (yields. 85% (23), 79-90% (21), 74-79% (7), 70% (18)) (19) (20) (22), or Cu powder (66% yield (24)) (25), or mere boilg. with HCl (26), or use of CuH (27), or  $CaCl_2$  (28) see indie. refs.; for prepn. from *o*-toluenediazonium chloride (solid) [Beil. XVI-495, XVI<sub>1</sub>-(358)] with  $C_6H_6$  +  $AlCl_3$  (29), from *o*-toluenediazonium chloroplatinate on htg. (30), or from *o*-toluenediazopiperidine by htg. with HCl (31) see indie. refs.; for prepn. of  $\bar{C}$  from *o*-cresol (1:1400) via conv. with  $PCl_5$  at 140° to *tris*-(*o*-toloxy)phosphoric acid dichloride and htg. of latter at 180° see (32); for prepn. of  $\bar{C}$  from *p*-toluenesulfonyl chloride via chlorination to 2-chlorotoluenesulfonyl chloride-4 followed by hydrolysis with 10%  $H_2SO_4$  (33) to 2-chlorotoluenesulfonic acid-4 (see below) and subsequent replacement of  $-SO_3H$  by H with superheated steam in 80%  $H_2SO_4$  (overall yield 88-90% (33)) cf. (34) (35); for prepn. of  $\bar{C}$  from 2-chlorotoluenesulfonic acid-5 (see below) or its sodium salt by steam distn. of its soln. in 75%  $H_2SO_4$  see (81).]

[For prepn. of  $\bar{C}$  from toluene with  $Cl_2$  in pres. of Fe (8) (36) (38), or  $I_2$  (37) (39), Fe +  $I_2$  (15), Al/Hg (45),  $MoCl_5$  (36),  $SbCl_5$  (39), or  $PbCl_2$  (8), from toluene via electrolysis of its suspension in boilg. HCl (40) or in HCl/AcOH at 35° (41), from toluene by boilg. with  $PbCl_2 \cdot 2NH_4Cl$  (42), from toluene with  $SO_2Cl_2$  + cat. (43) especially  $AlCl_3$  (43) (44), from toluene with *n*-butyl chlorosulfonate (46), from toluene with  $NCl_3$  (47) see indie. refs.: no *m*-chlorotoluene is formed by any of these methods, but the proportion of  $\bar{C}$  to its ac-

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ring-closes to give (92% yield (90)) (91) 2-chloro-3-methylanthraquinone, colorless tabs. from toluene, m.p.  $219^\circ$  (91) cor. (90); B, m.p.  $176-177^\circ$  (91), the minor prod., regarded (91) as *o*-(2-chloro-3-methylbenzoyl)benzoic acid, with conc.  $H_2SO_4$  ring-closes to give 1-chloro-2-methylanthraquinone, yel.-br. ndls. from toluene, m.p.  $171^\circ$  (91),  $170-171^\circ$  (90).] — [For reactn. of  $\bar{C}$  with 3,4-dichlorophthalic anhydride (3:3695) (92) or with pyromellitic anhydride (93) see indic. refs.]

[ $\bar{C}$  with aq. NaOH in pres. of Cu at  $350-360^\circ$  under press. yields (94) a mixt. contg. 41% *o*-cresol (1:1400) + 59% *m*-cresol (1:1730) (for extensive study of hydrolysis of  $\bar{C}$  as means of prepn. of *m*-cresol (1:1730) see (112));  $\bar{C}$  with  $NH_3$  + cat. under press. as directed (95) (96) (97) yields *o*-toluidine (for behavior of  $\bar{C}$  with liquid  $NH_3$  see (98)). —  $\bar{C}$  with aniline + Cu at  $175^\circ$  yields (99) phenyl-*o*-tolylamine. —  $\bar{C}$  with diphenylamine + K at  $240-245^\circ$  in  $H_2$  gives (by rearr.) (100) *N,N*-diphenyl-*m*-toluidine, m.p.  $69-70^\circ$ .] — [Note that  $\bar{C}$  does not react with aq. sodium sulfanilate +  $Na_2CO_3$  (dif. from benzyl chloride (3:8535)) and use in sepn. of  $\bar{C}$  from the latter (8)]

[ $\bar{C}$  on mononitration, e.g., with 4 pts.  $HNO_3$  ( $D = 1.52$ ) at  $0^\circ$  (101) gives a mixt. contg. all four possible isomers, viz., 43% 2-chloro-5-nitrotoluene [Beil. V-329,  $V_1$ -(163)], m.p.  $42.9^\circ$  (101),  $44^\circ$  (102), 21% 2-chloro-6-nitrotoluene [Beil. V-327,  $V_1$ -(162)], m.p.  $35.3^\circ$  (101),  $37^\circ$  (103) (104), 19% 2-chloro-3-nitrotoluene [Beil. V-328,  $V_1$ -(163)], m.p.  $22.1^\circ$  (101),  $21.5^\circ$  (105), and 17% 2-chloro-4-nitrotoluene [Beil. V-329,  $V_1$ -(163)], m.p.  $62.3^\circ$  (101),  $65^\circ$  (105A).]

$\bar{C}$  on dinitration, e.g., with mixt. of 3 wt. pts.  $HNO_3$  ( $D = 1.48$ ) + 9 wt. pts. conc.  $H_2SO_4$  at  $100^\circ$  (106), or with 2 vol. pts.  $HNO_3$  ( $D = 1.42$ ) + 5 vols. pts. conc.  $H_2SO_4$  at  $100^\circ$  as directed (107), gives mainly (55-60% (107)) 2-chloro-3,5-dinitrotoluene [Beil. V-345,  $V_1$ -(169)], cryst. from alc., m.p.  $64^\circ$  (107),  $63-64^\circ$  (106), accompanied by smaller amts. of three isomers, viz., 2-chloro-4,5-dinitrotoluene, m.p.  $83.5^\circ$  (18-20% (107)), 2-chloro-5,6-dinitrotoluene, m.p.  $106.5^\circ$  (18-20% (107)), and 2-chloro-4,6-dinitrotoluene, m.p.  $49^\circ$  (1-2% (107)) [the two other possible dinitro-2-chlorotoluenes have been prepd. by indirect means, viz., 2-chloro-3,4-dinitrotoluene, m.p.  $89^\circ$  (108), and 2-chloro-3,6-dinitrotoluene, m.p.  $62-63^\circ$  (109)].

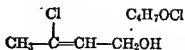
[ $\bar{C}$  on monosulfonation with fuming  $H_2SO_4$  (37) or 100%  $H_2SO_4$  (23) (8) or  $ClSO_3H$  (110) (see below) yields 2-chlorotoluenesulfonic acid-5 [Beil. XI-95];  $\bar{C}$  sulfonates more readily (8) than *p*-chlorotoluene (3:8287) and may thus be used to separate  $\bar{C}$  from the latter (8) (111).]

⑤ 2-Chlorotoluenesulfonamide-6 (4-chloro-3-methylbenzenesulfonamide-1): cryst. from dil. alc., m.p.  $126^\circ$  u.c. (110). [From  $\bar{C}$  with  $ClSO_3H$  as directed (110) followed by conv. of the intermediate 2-chlorotoluenesulfonyl chloride-5, cryst. from pet. ether, m.p.  $63^\circ$  u.c. (110), with  $(NH_4)_2CO_3$ .]

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## 3:8270 3-CHLOROBUTEN-2-OL-1

(2-Chlorobuten-2-ol-4;  
γ-chlorocrotonyl alcohol)C<sub>4</sub>H<sub>7</sub>OCl

Beil. S.N. 25

B.P. 161-162°	(1)	$D_4^{20} = 1.1139$	(1)	$n_D^{20} = 1.4678$	(1)
92-93° at 50 mm.	(2)		1.1128 (2)		1.4652 (3) (4)
92° at 50 mm.	(3) (4)				1.4649 (2)
78.5-79° at 25 mm.	(1)	$D_4^{17} = 1.1172$	(5)	$n_D^{17} = 1.4654$	(3)
67-67.5° at 12 mm.	(5)				
56.5° at 9 mm.	(6)	$D_4^{15} = 1.1185$	(1)	$n_D^{15} = 1.4698$	(1)

[For prepn. of  $\bar{C}$  from 1,3-dichlorobutene-2 (3:5550) by hydrolysis with steam (6), or aq. alk. (4) (6), or aq. K<sub>2</sub>CO<sub>3</sub> (2), aq. Na<sub>2</sub>CO<sub>3</sub> (70-80% yield (3)) or CaCO<sub>3</sub> (5) see indic. refs.; note that the ether corresp. to  $\bar{C}$  (see below) is always formed as a by-product (4) and also that alc. KOH does not yield  $\bar{C}$  but the corresponding ethers (see below); for prepn. of  $\bar{C}$  from 1-bromo-3-chlorobutene-3 ("chloroprene hydrobromide") by refluxing 2 hrs. with aq. Na<sub>2</sub>CO<sub>3</sub> (80% yield) see (1).]

$\bar{C}$  refluxed with 16% H<sub>2</sub>SO<sub>4</sub> yields (2) methyl vinyl ketone.

Ethers of  $\bar{C}$ . *Di-(3-chlorobuten-2-yl-1) ether*: from  $\bar{C}$  in aq. KOH by addn. of 1 mole 1,3-dichlorobutene-2 (3:5550) (80-90% yield (3)) (4); b.p. 142° at 50 mm., (3) (4)  $D_4^{20} = 1.171$  (3), 1.1171 (4);  $n_D^{20} = 1.4860$  (3) (4).

*Methyl 3-chlorobuten-2-yl-1 ether*: from 1,3-dichlorobutene-2 (3:5550) with MeOH + alk. (7), b.p. 125-120° (7).

*Ethyl 3-chlorobuten-2-yl-1 ether*: from 1,3-dichlorobutene-2 (3:5550) with excess conc. alk. EtOH (80-90% yield (3)) (4) (7); b.p. 143° (3) (4), 88-89° at 120 mm. (7), 62-64° at 40 mm. (3) (4);  $D_4^{20} = 0.9788$  (7),  $D_4^{20} = 0.9729$  (3) (4);  $n_D^{20} = 1.4392$  (7), 1.4382 (3) (4).

*Phenyl 3-chlorobuten-2-yl-1 ether*: from 1,3-dichlorobutene-2 (3:5550) with alk. + phenol (7); b.p. 94° at 1 mm.,  $D_4^{20} = 1.1080$ ,  $n_D^{20} = 1.5378$  (7).

Esters of  $\bar{C}$ . *S-Chlorobuten-2-yl-1 acetate*: from  $\bar{C}$  with AcCl (1); b.p. 80.5-81.5° at 25 mm.  $D_4^{20} = 1.1020$ ,  $n_D^{20} = 1.4495$  (1).

$\bar{C}$  readily adds Br<sub>2</sub> yielding (1) 2,3-dibromo-3-chlorobutanol-1, b.p. 111-112.5° at 10 mm.,  $D_4^{20} = 2.0058$ ,  $n_D^{20} = 1.5544$  (1).

① 3-Chlorobuten-2-yl-1 N-(α-naphthyl)carbamate: cryst. from lgr., m.p. 107-108° (5).

② 3-Chlorobuten-2-yl-1 3,5-dinitrobenzoate: m.p. 72-73° (6).

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3:8250 1-CHLOROHEPTANE  $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{Cl}$   $\text{C}_7\text{H}_{15}\text{Cl}$  Beil. I - 154  
(*n*-Heptyl chloride)  $\text{I}_1$ -( 56)  
 $\text{I}_2$ -(117)

B.P.		F.P.	
159.5° (1)	at 769 mm. (10)	-69.5° (6)	$D_4^{20} = 0.8766$ (10)
159.2°	at 750 mm. (2)		0.8725 (6)
158.8-160.0°	(3)		$n_D^{20} = 1.42844$ (4)
158.5-159.5°	(4)		1.42571 (10)
117.0-117.5° cor.	at 163 mm. (5)		$D_4^{15} = 0.8783$ (6)
61.4°	at 27 mm. (6)		

[For prepn. of  $\bar{C}$  from heptanol-1 (1:6240) by shaking 2 days with conc.  $\text{HCl} + \text{ZnCl}_2$  in cold (60% yield (4)) see (4) (8); with  $\text{PCl}_3 + \text{ZnCl}_2$  (70% yield),  $\text{PCl}_5 + \text{ZnCl}_2$  (78% yield), or  $\text{SOCl}_2 + \text{pyridine}$  (81% yield) see (4); with  $\text{SOCl}_2$  but without pyridine (80% yield) see (10), with conc.  $\text{HCl}$  in s.t. at 120-130° see (2); with  $\text{HCl}$  over  $\text{Al}_2\text{O}_3$  at 420-440° see (7); for formation from *n*-heptylamine +  $\text{NOCl}$  see (8); for formation during chlorination of *n*-heptane see (9).]

[For study of reaction of  $\bar{C}$  with  $\text{KI}$  in acetone see (5); for difficulty in forming  $\text{R.MgCl}$  see (1); note, however, that  $\bar{C}$  with  $\text{Mg}$  in dry ether + trace  $\text{I}_2$  gives (97.5% yield (11))  $\text{RMgCl}$ .]

③ *N*-(*n*-Heptyl)tetrachlorophthalimide: lifts from  $\text{EtOH}$ , m.p. 145-146° (12). [From  $\bar{C}$  (7) or from *n*-heptyl bromide with  $\text{K}$  tetrachlorophthalimide (12).]

3:8250 (1) Underwood, Gale, *J. Am. Chem. Soc.* 66, 2117-2120 (1934). (2) Cross, *Ann.* 189, 3 (1877). (3) Kohlrausch, Köppl, *Monatsh.* 63, 268 (1933). (4) Clark, Streight, *Trans. Roy. Soc. Can.* (3) 23, III 77-83 (1929). (5) Conant, Hussey, *J. Am. Chem. Soc.* 47, 485 (1925). (6) Sherrill, *J. Am. Chem. Soc.* 52, 1985-1988 (1930). (7) Sabatier, Mailhe, *Compt. rend.* 169, 124 (1919). (8) Esolonina, *Cent.* 1898, II 888. (9) Wertyporoch, *Ber.* 66, 737-738 (1933). (10) Vogel, *J. Chem. Soc.* 1943, 638, 640.  
(11) Houben, Boedler, Fischer, *Ber.* 69, 1768, 1777 (1936). (12) Allen, Nicholls, *J. Am. Chem. Soc.* 56, 1409-1410 (1934).

3:8264 METHYL *d,l*- $\alpha$ -CHLORO-*n*-VALERATE  $\text{C}_6\text{H}_{11}\text{O}_2\text{Cl}$  Beil. II - 302  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{COOCH}_3)$   
 $\text{Cl}$   $\text{H}_1$ -  
 $\text{H}_2$ -

B.P. 160° at 764 mm. (1)

[For prepn. of  $\bar{C}$  from  $\alpha$ -chloro-*n*-valeronitrile with  $\text{MeOH} + \text{H}_2\text{SO}_4$  see (1).]

3:8264 (1) Henry, *Bull. acad. roy. Belg.* (3) 36, 241-262 (1898); *Cent.* 1898, I 194.

[For study of system:  $\bar{C}$  +  $SbCl_5$  see (7).]

[ $\bar{C}$  with  $NH_3$  + cat. as directed (34) (35) yields *m*-toluidine;  $\bar{C}$  with aq.  $NaOH$  in pres. of  $Cu$  at 300–400° under press. yields (51) mixt. of *o*-cresol (1:1400), *m*-cresol (1:1730), and *p*-cresol (1:1410).]

[ $\bar{C}$  on mononitration, e.g., with 4 pts.  $HNO_3$  ( $D = 1.52$ ) nt 0°, gives a mixt. contg. (36) cf. (37) (13) (38) 59% 3-chloro-6-nitrotoluene [Beil. V-327,  $V_1$ -(162)], m.p. 24.9°, + 32% 3-chloro-4-nitrotoluene [Beil. V-329,  $V_1$ -(163)], m.p. 24.2°, + 9% 3-chloro-2-nitrotoluene [Beil. V-327,  $V_1$ -(162)], m.p. 23.4°. —  $\bar{C}$  on dinitration, e.g., with mixt. of 2 wt. pts.  $HNO_3$  ( $D = 1.52$ ) + 3 wt. pts. conc.  $H_2SO_4$  at room temp. for 12–18 hrs. (13), gives (95.8% yield (13)) 3-chloro-4,6-dinitrotoluene [Beil. V-344,  $V_1$ -(168)], cryst. from alc. or lgr., m.p. 91° (13) (38) (39), 90–90.5° (52) (note that the isomeric 3-chloro-2,6-dinitrotoluene [Beil.  $V_1$ -(168)] (40), m.p. 77° (40), and 3-chloro-2,4-dinitrotoluene, m.p. 92° (41), are also known but prepd. by indirect means). —  $\bar{C}$  on trinitration, e.g., by refluxing with 3 pts  $HNO_3$  (49.4°Bé) + 3 pts.  $H_2SO_4$  (66°Bé) at 160° (42), yields 3-chloro-2,4,6-trinitrotoluene [Beil. V-349], cryst. from  $C_6H_6$  + lgr., m.p. 150–151° (52), 148.5° (42).]

[ $\bar{C}$  with  $Na$  followed by  $CO_2$  as directed gives (yields: 88% (43A), 58% (43B)) *m*-toluic acid (1:0705), m.p. 110–111°, also obtd. in small yield (44) from  $\bar{C}$  + alc.  $KCN$  in pres. of  $NiCl_2$ , htd. in s.t. at 260–270° for 20 hrs.]

[ $\bar{C}$  with  $CrO_2Cl_2$  gives a cpd. which with aq. gives (44.5% yield (45)) *m*-chlorobenzaldehyde (3:6475).]

$\bar{C}$  on oxidn. with  $K_2Cr_2O_7$  +  $H_2SO_4$  (14), with 5% aq.  $KMnO_4$  (11) (46) or with dil.  $HNO_3$  in s.t. at 130–140° for 10 hrs. (15) gives (75% yield (46)) *m*-chlorobenzoic acid (3:4392).

③ 3-Chloro-6-sulfonamidotoluene (4-chloro-2-methylbenzenesulfonamide): cryst. from dil. alc., m.p. 184–185° u.c. (47). [From  $\bar{C}$  with  $ClSO_3H$  as directed (47) followed by treatment of the resultant 4-chloro-2-methylbenzenesulfonyl chloride, cryst. from pet. eth., m.p. 52–53° u.c. (47), 54° (49) with  $(NH_4)_2CO_3$ .]

3:8275 (1) Feitler, *Z. physik. Chem.* 4, 73–76 (1889). (2) Norris, Turner, *J. Am. Chem. Soc.* 61: 2128–2131 (1939). (3) Kohlrausch, Pongratz, *Monatsh.* 63, 441 (1934). (4) Stuckey, Saylor, *J. Am. Chem. Soc.* 62, 2923 (1940). (5) Wibaut, *Rec. trav. chim.* 32, 286 (1913). (6) Rule, McLean, *J. Chem. Soc.* 1931, 689. (7) Menschutkin, *J. Russ. Phys.-Chem. Soc.* 44, 1940 (1912); *Cent.* 1913, I 805. (8) Haase, *Ber.* 26, 1053 (1893). (9) Seubert, *Ber.* 22, 2520, 2522 (1889).

(10) Wibaut, *Rec. trav. chim.* (1900). (11) Wroblewski, *Ann.* 3-1059 (1892). (12) Klages, *Ber.* -3023 (1894). (13) Autenrieth, 1009 (1916). (14) Willstätter,

(15) Cohen, Dakin, *J. Chem. Soc.* 79, 1117–1118 (1901). (16) Jenkins, *J. Am. Chem. Soc.* 55, 2897 (1933). (17) Sampey, Fawcett, Morehead, *J. Am. Chem. Soc.* 62, 1839–1840 (1940). (18) Thompson, *Stann. J. Chem. Soc.* 1913, 105, 1911–1912.

(19) au, *Compt. rend.* 1911, 105, 1911–1912. (20) Albert, *Cent.* 1931,

11 908.

(21) I.G., *Brit.* 394,995, Aug. 3, 1933; *Cent.* 1933, II 2753. (22) Houben, Fischer, *Ber.* 64, 2649 (1931). (23) Kunckell, *Ber.* 4, 2649 (1871). (24) Houben, Fischer, *Ber.* 64, 2649 (1931). (25) May 5, 1932; *Cent.* 1932, II 1237. (26) 10, 1934; *Cent.* 1934, II 1846. (27) (36) *Chem. Soc.* 38, 1327–1333 (1916).

(28) (1900). (29) Sane, Joshi, *J. Indian. Chem. Soc.* 5, 300 (1928). (30) Lindemann, Pabst, *Ann.* 462, 43 (1928).

(31) Brady, Bowman, *J. Chem. Soc.* 119, 896–897 (1921). (32) Réverdin, Dresel, Déletra,

3:8275 *m*-CHLOROTOLUENE $C_7H_7Cl$ 

Beil. V - 291

V<sub>1</sub>-(150)V<sub>2</sub>-(226)

B.P.		F.P.	
162.2°	at 766.5 mm. (1)	-48.0° (7)	$D_4^{20} = 1.07218$ (9)
161.8-162°	at 768 mm. (2)	(6)	$n_D^{15-20} = 1.5214$ (9)
161.8-161.9°	(3)	-47.8° (8)	$D_4^{18.7} = 1.0760$ (10)
161.74-161.75°	at 760 mm. (4)		$n_D^{19.7} = 1.52252$ (10)
161.6°	at 760 mm. (5)		$D_4^{13.9} = 1.0797$ (10)
45.5°	at 12 mm. (6)		$n_D^{13.9} = 1.52535$ (10)

[For prepn. of  $\bar{C}$  from *m*-toluidine [Beil. XII-853, XII-(397)] via diazotization and use of  $Cu_2Cl_2$  reactn. (yields: 86% (46), 80% (11)) (12) (13) or  $CuH$  (35% yield (48)) see indic. refs., from 3-chloro-4-aminotoluene [Beil. XII-939, XII-(436)] via diazotization followed by boilg. with alc. (60% yield (14)) or conversion to corresp. hydrazine and subsequent oxidn. with  $CuSO_4$  (50% yield (15)) see indic. refs.; from 5-chloro-2-aminotoluene [Beil. XII-335] with alc.  $H_2SO_4$  + ethyl nitrite (1) or by diazotization, reduction to the corresp. hydrazine, and oxidn. of latter with  $CuSO_4$  (43-63% yield (15)) see indic. refs.; for formn. of  $\bar{C}$  from 1-methylcyclohexanone-3 by conversion with  $PCl_5$  to 3-chloro-1-methylcyclohexene-2, treatment with  $Br_2$ , and boilg. with quinoline see (16); from 3-chloro-1-methylcyclohexadiene-1,3 [Beil. V-116] by conv. to dibromide and boilg. with quinoline see (17), from *m*-cresol (1:1730) with  $PCl_5$ , or from tri-(*m*-tolyl) phosphate at 210° see (18); for study of formn. of  $\bar{C}$  by partial rearr. with  $AlCl_3$  of *o*-chlorotoluene (3:8245) or *p*-chlorotoluene (3:8287) see (2).]

[ $\bar{C}$  with  $H_2$  in pres. of  $Pd/CaCO_3$  in alc./alk. soln. loses all its chlorine as  $HCl$  (19);  $\bar{C}$  with  $H_2$  in pres. of  $Pt$  in  $AcOH$  loses  $HCl$ , but no quant. data are given (20).]

[ $\bar{C}$  with  $Cl_2$  in pres. of  $Al/Hg$  yields (21) both 2,5-dichlorotoluene (3:6245) and 3,4-dichlorotoluene (3:6355) but no trace of any other isomers.]

[ $\bar{C}$  with  $Br_2$  in  $CCl_4$  at 60-80° in bright light (22) (23) or in  $CS_2$  (23) or  $\bar{C}$  at 130° with  $Br_2$  directly (24) gives (55% yield (22)) *m*-chlorobenzyl bromide, m p. 15-15.5°, b p. 103-105° at 8 mm. (22), b.p. 103-111° at 10 mm (24),  $D_4^{25} = 1.5652$  (22);  $\bar{C}$  with  $Br_2$  in  $CCl_4$  in pres. of  $Al/Hg$  (25) or  $\bar{C}$  with  $Br_2$  in  $AcOH$  in pres. of  $HNO_3$  or  $HNO_3/H_2SO_4$  (26) gives both 6-bromo-3-chlorotoluene, b.p. 120-125° at 15 mm. (26), 100-103° at 15 mm. (25) (note disagreement!), and 4-bromo-3-chlorotoluene, b.p. 90-93° at 12 mm. (26).] — [ $\bar{C}$  with  $Br_2$  in pres. of  $Be$  yields (27)  $\alpha,\gamma$ -dibromo-3-chlorotoluene, m.p. 96.5°.]

[ $\bar{C}$  with  $AlCl_3$  +  $HCl$  gas as directed undergoes partial rearr. (2) to both *o*-chlorotoluene (3:8245) and *p*-chlorotoluene (3:8287), for anal. of mixtures of the three isomers see (2).]

[ $\bar{C}$  with  $AcCl$  +  $AlCl_3$  in  $CS_2$  gives (60% yield (28)) 3-chloro-4-acetyltoluene (2-chloro-4-methylacetophenone), b.p. 260-262° at 760 mm. (28), b.p. 120-126° at 14 mm (29), accompanied (29) by some of the isomeric 3-chloro-6-acetyltoluene (4-chloro-2-methylacetophenone), b.p. 120-122° at 14 mm. (29). —  $\bar{C}$  with chloroacetyl chloride (3:5235) +  $AlCl_3$  in  $CS_2$  gives (70% yield (33)) 3-chloro-6-(chloroacetyl)toluene ( $\omega$ ,4-dichloro-2-methylacetophenone, m.p. 90° (33). —  $\bar{C}$  with  $\beta$ -chloropropionyl chloride (3:5690) +  $AlCl_3$  in  $CS_2$  gives (87% yield (50)) (30) 3-chloro-6-( $\beta$ -chloropropionyl)toluene which on ring closure with conc.  $H_2SO_4$  gives (50) (30) 5-chloro-7-methylindanone-1, m.p. 71° (50) (30). —  $\bar{C}$  with biphenyl-4,4'-bis-(carboxylic acid chloride) +  $AlCl_3$  yields (31) 4,4'-bis-(4-chloro-2-methylbenzoyl)-biphenyl (used in prepn. of bis-anthraquinonyl derivs.)]

[ $\bar{C}$  with trichloroacetonitrile +  $AlCl_3$  as directed (32) yields 4-chloro-2-methylbenzoic acid (3:4700).]



[Other reactns. involving only the OH group of  $\bar{C}$  include the following:  $\bar{C}$  with acetylene +  $BF_3$  +  $HgO$  gives (38% yield (30)) ethylidene bis-( $\gamma$ -chloro-*n*-propyl)acetal, b.p. 127-129° at 14 mm. (30);  $\bar{C}$  with benzonitrile +  $HCl$  gas in ether gives (31)  $\gamma$ -chloro-*n*-propyl iminobenzoate hydrochloride;  $\bar{C}$  with  $\beta$ -acetohomoglucose +  $Ag_2CO_3$  yields (32) tetra-acetyl- $\beta$ -d-( $\gamma$ -chloro-*n*-propyl)glucoside, m.p. 74° (for extension to prepn. of corresp. xyloside, galactoside, and lactoside see (32)).]

[ $\bar{C}$  with solid  $KOH$  loses  $HCl$  on htg. giving (16) (7) (10) (1) 1,3-epoxypropane (trimethylene oxide) [Beil. XVII-6, XVII-3]], b.p. 47.8° at 760 mm.,  $D_4^{25} = 0.8930$ ,  $n_D^{25} = 1.3897$  (16) (for study of rate of reactn. see (33)).]

[ $\bar{C}$  with  $NaOEt$  in abs. alc. reacts vigorously giving (38% yield (34)) ethyl  $\gamma$ -hydroxy-*n*-propyl ether (trimethylene glycol monoethyl ether) [Beil. I-476, I-(247)], b.p. 160-161° (34), 162.1-162.2°,  $D_4^{20} = 0.91691$ ,  $n_D^{20} = 1.41666$  (35), accompanied by some trimethylene glycol diethyl ether, b.p. 140° (34). —  $\bar{C}$  with  $NnSH$  as directed gives (70-80% yield (34))  $\gamma$ -hydroxy-*n*-propyl mercaptan, b.p. 85-90° at 15 mm. ( $Hg$  mercaptide =  $Hg(SCH_2CH_2CH_2OH)_2$ , pl. from butanol, m.p. 132-134° (36). —  $\bar{C}$  with aq.  $Na_2S$  gives (36) bis-( $\gamma$ -hydroxy-*n*-propyl) sulfide, visc. oil which could be neither distd. nor crystd. but which with phenyl isocyanate gave the corresp. bis-(phenylcarbamate), m.p. 146-148° (36). —  $\bar{C}$  with  $NaSCH_3$  in ether gives (76% yield (42))  $\gamma$ -hydroxy-*n*-propyl methyl sulfide, b.p. 105-105.5° at 30 mm. (42). —  $\bar{C}$  with benzyl mercaptan in alc. gives (88% yield (43)) benzyl  $\gamma$ -hydroxy-*n*-propyl sulfide, b.p. 185° at 19 mm. (43).]

[ $\bar{C}$  in alk. medium reacts with phenols yielding corresp. subst. alcohols; e.g.,  $\bar{C}$  with phenol + alc.  $NaOEt$  (75% yield (37)) or  $\bar{C}$  + phenol + aq.  $NaOH$  (80% yield (38) (39)) gives 3-phenoxypropanol-1, b.p. 153-160° at 25 mm.,  $n_D^{20} = 1.491$  (37) which with  $ZnCl_2$  at 215° loses aq. and ring-closes (37) to chromane [Beil. XVII-52, XVII-(22)]; for corresp. reactn. with *o*-cresol (40), with *m*-cresol (41), *p*-cresol (41),  $\beta$ -naphthol (40), or resorcinol (40) see indic. refs.]

[ $\bar{C}$  with prim. or sec. amines splits out  $HCl$  yielding corresp. subst. aminoalcohols; e.g., for reactn. of  $\bar{C}$  with aniline + anhydrous  $Na_2CO_3$  giving (67.5% yield) 3-(*N*-phenylamino)propanol-1 (37) (4 hydroxy- $\gamma$ -phenylamino) b.p. 102° at 20 mm.,  $D_{28}^{25} = 1.063$ ,  $n_D^{25} = 1.4743$ ,  $n_D^{20} = 1.4762$ , see (76); for  $\bar{C}$  with acetone + sec. amines see (47) (55); for  $\bar{C}$  with morpholine giving (75% yield) 3-(morpholino)propanol-1, b.p. 147-149° at 21 mm.,  $n_D^{25} = 1.4743$ ,  $n_D^{20} = 1.4762$ , see (76); for  $\bar{C}$  with piperidine see (48) (56).] —

[ $\bar{C}$  with *ter*-amines yields corresp. quat. ammon. salts; e.g.,  $\bar{C}$  with  $(CH_3)_3N$  in  $C_6H_6$  in s.t. at 100° for 8 hrs. gives (92% yield (49))  $\gamma$ -homocholine chloride, m.p. 173° (49);  $\bar{C}$  with pyridine gives (85% yield (50))  $\gamma$ -hydroxy-*n*-propyl pyridinium chloride, oil.] — [For reactn. of  $\bar{C}$  with arsanilic acid (*p*-aminobenzenearsonic acid) (51), with *p*-hydroxybenzenearsonic acid (52), with ethyl  $\beta$ -methylaminopropionate (53), or with various carbazole derivs. (54) see indic. refs.]

[ $\bar{C}$  with 1 mole thiourea htd. at 120-125° yields (57) *S*-( $\gamma$ -hydroxy-*n*-propyl)isothiourrea hydrochloride, cryst. from butanol, m.p. 130° (57);  $\bar{C}$  with dry sodium *p*-toluenesulfonamide htd. at 160-170° for 18 hrs. yields (58) *N*-( $\gamma$ -hydroxy-*n*-propyl)-*p*-toluenesulfonamide as an oil.]

[For study of rate of reactn. of  $\bar{C}$  with  $KI$  in acetone at 35° and 45° see (39); for reactn. of  $\bar{C}$  with  $Na_3AsO_3$  see (5).]

—  $\gamma$ -Chloro-*n*-propyl acetate [Beil. II-(48), II-(139)]: liq., b.p. 168-169° (59), 165-166° (60), 88-90° at 22 mm. (61), 66° at 14 mm. (17), 62-63° at 10 mm. (7)  $D_{21}^{25} = 1.1105$  (7);  $n_D^{25} = 1.431$  (7). [From  $\bar{C}$  +  $AcCl$  (yields: 90% (60), 87% (16)) (7) (62), from 1,3-dichloropropane (3:5450) with  $AgOAc$  (53% yield (61)), or from

*Ber.* 37, 2091-2095 (1904); *Bull. soc. chim.* (3) 31, 633 (1904). {43A} Morton, LeFevre, Hechenbleikner, *J. Am. Chem. Soc.* 58, 754-755 (1936). {43B} Morton, Stevens, *J. Am. Chem. Soc.* 63, 4031-4032 (1931). {44} Siebodziński, *J. prakt. Chem.* (2) 143, 119 (1935). {45} Law, Perkin, *J. Chem. Soc.* 93, 1836 (1908). {46} Koopal, *Rec. trav. chim.* 34, 144 (1915). {47} Huntress, Carten, *J. Am. Chem. Soc.* 62, 512-513 (1940). {48} Neogi, Mitra, *J. Chem. Soc.* 1928, 1332. {49} I.G., *Brit.* 281,290, Nov. 22, 1927; French 644,319, Oct. 5, 1928; *Cent.* 1929, II 352. {50} Mayer, Müller, *Ber.* 60, 2281-2283 (1927).

{51} Britton (to Dow Chem. Co.), U.S. 1,996,744, April 9, 1935; *Cent.* 1935, II 1962. {52} Qvist, Moilanen, *Acta Acad. Aboensis, Math. et Phys.* 14, No. 3, 9 pp. (1943); *Cent.* 1943, II 1268-1269; *C.A.* 38, 5491 (1944).

3:8285 3-CHLOROPROPANOL-1  $\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$   $\text{C}_3\text{H}_7\text{OCl}$  *Beil.* I - 356  
(Trimethylene chloro-  $\begin{array}{c} | \\ \text{Cl} \end{array}$   $\text{I}_1$ -(180)  
hydrin,  $\gamma$ -chloro- $n$ -  $\text{I}_2$ -(370)  
propyl alcohol)

## B.P.

160-162° cor.	(1) (10)	$D_4^{20} = 1.1318$ (9)	$n_D^{20} = 1.44693$ (2)
160.0-160.3° at 734.1 mm.	(2)	1.1309 (2)	1.4460 (9)
158.6-161.0° at 734 mm.	(3)	1.1262 (7)	1.448 (7)
158-159°	(4)		
74-76° at 23 mm.	(5)	$D_4^{15} = 1.129$ (10)	
66.0-66.2° at 16 mm.	(6)		
63-64° at 16 mm.	(7)		
64-66° at 14 mm.	(77)		
60-64° at 10 mm.	(8)		
53° at 6 mm.	(2)		

Colorless oil with agreeable odor; undergoes partial decompn. on distn. at ord. press. — Very sol. aq. but not miscible with it.

[For prepn. of  $\bar{C}$  from propanediol-1,3 (trimethylene glycol) (1.6490) with HCl gas (50-60% yield (8)) {4} {7} {11} {12} {13} {1}, with conc. HCl (yield: 34% {14}, 28% {15}, 15% {16}) (some 1,3-dichloropropane and other prods. are also formed), with  $\text{SOCl}_2$  (50-60% yield (77)), or with  $\text{S}_2\text{Cl}_2$  (yields: 68% (5), 60% (16)) (17) see indic. refs.; for formn. of  $\bar{C}$  from  $\gamma$ -chloro- $n$ -propyl acetate (see below) by alcoholysis with MeOH/HCl (85% yield (18)) or from  $\gamma$ -chloro- $n$ -propyl trichloroacetate (9) by hydroly. with aq. KOH at 35° (9) see indic. refs.; for manuf. from ethylene + formaldehyde + HCl +  $\text{ZnCl}_2$  see (19).]

$\bar{C}$  on oxidn. with conc.  $\text{HNO}_3$  gives (yields: 78-79% (20), 54-56% (21), 30-40% (13))  $\beta$ -chloropropionic acid (3.0460) (note that the presumably intermediate  $\beta$ -chloropropionaldehyde (3:5576) is best obtd. by other means).

[ $\bar{C}$  with HBr gas (22), on distn. with 48% HBr (yield: 75-85% (22), 40% (11)), with HBr +  $\text{H}_2\text{SO}_4$  (yield: 89% (23)), or with  $\text{PBr}_3$  (94% yield (11)) gives 1-bromo-3-chloropropane (trimethylene chlorobromide) (*Beil.* 1-109,  $\text{I}_1$ -(36),  $\text{I}_2$ -(75)), b.p. 142-145°,  $D_4^{25} = 1.4718$  (24),  $n_D^{25} = 1.4732$  (24); for study of rate of reactn. of  $\bar{C}$  with HBr in phenol see (25).]

[ $\bar{C}$  refluxed with  $\frac{1}{2}$  wt. conc.  $\text{H}_2\text{SO}_4$  gives (10-15% yield (26)) bis-( $\gamma$ -chloro- $n$ -propyl) ether, b.p. 215° at 745 mm.,  $D_4^{20} = 1.140$  (26) —  $\bar{C}$  with  $\text{SO}_2\text{Cl}_2$  gives (68% yield (27))  $\gamma$ -chloro- $n$ -propyl chlorosulfonate, b.p. 85° at 4 mm.,  $D_4^{20} = 1.456$  (27). —  $\bar{C}$  with  $\text{SOCl}_2$  gives (70% yield (27)) sym.-bis-( $\gamma$ -chloro- $n$ -propyl) sulfite, h.p. 161-162° at 13 mm.,  $D_4^{20} = 1.313$  (27).]

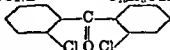
[ $\bar{C}$  with  $\text{COCl}_2$  (3:5000) directly (28) or in toluene (29) gives (43% yield (29))  $\gamma$ -chloro- $n$ -propyl chloroformate (3:6895);  $\bar{C}$  with trichloroacetic acid (3.1150) gives (57% yield (9))  $\gamma$ -chloro- $n$ -propyl trichloroacetate, b.p. 107° at 8 mm.,  $D_4^{15} = 1.4732$ ,  $n_D^{15} = 1.4830$  (9); for formn. of other esters (as derivs.) see below.]

berg, Bailar, *J. Am. Chem. Soc.* **51**, 2231 (1929). (17) Meisenheimer, Meis, *Ber.* **57**, 295 (1924). (18) Cathcart, Meyer, *Ber.* **25**, 1498, 3295 (1892). (19) Montagne, *Rec. trav. chim.* **26**, 266 (1907). (20) Britton, Moyle, Bryner (to Dow Chem. Co.), U.S. 2,377,751, June 5, 1945; C.A. **39**, 4097 (1945).

## 3: 0717 2,2'-DICHLOROBENZOPHENONE

(Di-(*o*-chlorophenyl) ketone) $C_{12}H_8OCl_2$ 

Beil S.N. 652



M.P. 45.4-46.6° cor. (1) B.P. 127-135° at 1 mm. (1)  
45-46° (1)

[For prepn. of  $\bar{C}$  from 2,2'-dichlorobenzilic acid (1) by oxidn. with  $CrO_3/AcOH$  (47% yield (1)) or from di-(*o*-chlorophenyl)carbinol (1) by oxidn. with  $Na_2Cr_2O_7/H_2SO_4/AcOH$  see indic. refs.]

② 2,2'-Dichlorobenzophenone 2,4-dinitrophenylhydrazone: m.p. 206-208° (1).

3: 0717 (1) Haller, Bartlett, Drake, Newman, Cristol et al., *J. Am. Chem. Soc.* **67**, 1600-1601 (1945).

## 3: 0720 ETHYLENE GLYCOL bis-CHLOROACETATE

 $C_6H_{10}O_4Cl_2$ 

Beil S.N. 160

 $ClCH_2.CO.O.CH_2$ 

$$\begin{array}{c} | \\ ClCH_2.CO.O.CH_2 \end{array}$$

M.P. 45-46.5° (1) B.P. 142-144° at 2 mm. (1)

Cryst. from ether/pet. eth. — Insol. aq. (dif. from  $\beta$ -hydroxyethyl chloroacetate (3:6780)).

[For prepn. of  $\bar{C}$  from ethylene oxide (1:6105) with chloroacetic acid (3:1370) as by-product of prepn. of  $\beta$ -hydroxyethyl chloroacetate (3:6780) see (1); note also that  $\bar{C}$  is formed (together with ethylene glycol (1:6165)) by disproportionation of  $\beta$ -hydroxyethyl chloroacetate (3:6780) on long stdg. in ord. glass bottles (1).]

$\bar{C}$  on shaking with aq. is hydrolyzed only very slowly (1).

[For use of  $\bar{C}$  as insecticide, fungicide, and disinfectant see (2).]

3: 0720 (1) Meerwein, Sönke, *J. prakt. Chem.* (2) **137**, 316-318 (1933). (2) Peet (to Rohm and Haas Co.), U.S. 1,816,441, July 28, 1931; *Cent.* **1932**, I 1146; C.A. **25**, 5501 (1931); French 667,633, Oct. 18, 1929; *Cent.* **1930**, I 2614.

trimethylene glycol (1:6490) with  $\text{Ac}_2\text{O} + \text{S}_2\text{Cl}_2$  (68% yield (17)).] — [This acetate with solid KOH loses HOAc giving (16) (7) (61) 2,3-epoxypropane (trimethylene oxide) (see above).]

—  $\gamma$ -Chloro-*n*-propyl benzoate: oil, b.p. 154–156° at 22 mm. (31), 155–156° at 15 mm. (4), 133–134° at 2 mm. (39),  $D_4^{22} = 1.1672$  (31),  $n_D^{20} = 1.5136$  (31). [From  $\bar{\text{C}} + \text{BzCl}$  (yields: 84% (39), 75% (4)) or from  $\gamma$ -chloro-*n*-propyl iminobenzoate hydrochloride (see above) by hydrol. (31).] — [For reactn. of this ester with pyrrolidine (63), pyrroline (63), piperidine (56), aubat. piperidines (64) (65) (68), hydrogenated quinolines (66), or with *N*-methyl-phenyl-alkylamines (67) see indic. refs.]

—  $\gamma$ -Chloro-*n*-propyl *p*-nitrobenzoate: oil, b.p. 163.5–169.5° at 2 mm.,  $D_{25}^{25} = 1.3222$ ,  $n_D^{25} = 1.54736$  (67). [From  $\bar{\text{C}} + p$ -nitrobenzoyl chloride on htg. (67).]

⑥  $\gamma$ -Chloro-*n*-propyl 3,5-dinitrobenzoate: colorless pl. from lt. pet., m.p. 77° (17). [From  $\bar{\text{C}} + 3,5$ -dinitrobenzoyl chloride (17).]

—  $\gamma$ -Chloro-*n*-propyl hydrogen phthalate: unreported.

—  $\gamma$ -Chloro-*n*-propyl hydrogen 3-nitrophthalate: unreported.

—  $\gamma$ -Chloro-*n*-propyl benzene sulfonate: unreported.

—  $\gamma$ -Chloro-*n*-propyl *p*-toluenesulfonate: oil, b.p. 216–219° at 17 mm. (69), 188–192° at 5 mm (24),  $D_4^{20} = 1.2674$  (69),  $D_{25}^{25} = 1.2396$  (24),  $n_D^{20} = 1.5230$  (69),  $n_D^{25} = 1.5225$  (24). [From  $\bar{\text{C}} + p$ -toluenesulfonyl chloride on htg. (69) or with aq. NaOH at 15° (50–55% yield (24)).] — [For reactn. of this ester with  $\text{RMgX}$  cpds. see (69) (24), with various sodium acetylides see (70).]

—  $\gamma$ -Chloro-*n*-propyl carbamate: pearly cryst. from hot. aq., m.p. 62° (29). [From  $\bar{\text{C}}$  with urea nitrate (2 moles) on htg. at 130–135° (16% yield (29)) or from  $\gamma$ -chloro-*n*-propyl chloroformate (3:6010) with conc. aq.  $\text{NH}_4\text{OH}$  (29).]

—  $\gamma$ -Chloro-*n*-propyl *N*-(phenyl)carbamate: ndls. from alc., m.p. 35° (29), m.p. 35–36° (28), b.p. 190° at 3.5 mm. (28). [From  $\bar{\text{C}} + \text{phenyl isocyanate at } 150^\circ$  (29) or from  $\gamma$ -chloro-*n*-propyl chloroformate (3:6010) with aniline (29).]

—  $\gamma$ -Chloro-*n*-propyl *N*-(*p*-nitrophenyl)carbamate: unreported.

⑦  $\gamma$ -Chloro-*n*-propyl *N*-( $\alpha$ -naphthyl)carbamate, cryst. from hot lgr., m.p. 78° (71) (17), 76.5° (9), 75.5–76.5° (28). [From  $\bar{\text{C}} + \alpha$ -naphthyl isocyanate (71).]

⑧ *N*-( $\gamma$ -Hydroxy-*n*-propyl)phthalimide [3-(*N*-phthalimido)propanol-1] [Beil. XXI-472]: cryst. from aq., m.p. 75° (72), 74° (73), 88° (74). [From  $\bar{\text{C}} + \text{K phthalimide at } 190^\circ$  (73); also indirectly as cited in other indicated refs.]

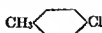
⑨ *N*-( $\gamma$ -Hydroxy-*n*-propyl)tetrachlorophthalimide [3-(*N*-tetrachlorophthalimido)propanol-1]: pr. from acetone, m.p. 165–166° (75). [From  $\bar{\text{C}}$  with K tetrachlorophthalimide as directed (75).]

3:8285 (1) Reboul, *Ann. chim.* (5) 14, 493–496 (1878). (2) Karvonen, *Ann. Acad. Sci. Fennicae A-3*, No. 7, 1–103, Cent. 1912, II 1271, C.A. 14, 2175–2176 (1920); *Ann. Acad. Sci. Fennicae A-5*, No. 6, 120. (3) Kohlräusch, Ypsilanti, *Z. physik. Chem.* B-32, 414 (1936). (4) Zaki, *J. Chem. Soc.* 1930, 2271. (5) Gough, King, *J. Chem. Soc.* 1928, 2439. (6) Smyth, Walls, *J. Am. Chem. Soc.* 54, 2253 (1932). (7) Lespiau, *Bull. soc. chim.* (5) 7, 254–255 (1940). (8) Marvel, Calvery, *Org. Syntheses*, Coll. Vol. 1 (2nd ed.), 533–535 (1941); (1st ed.), 519–521 (1932); 8, 112–115 (1928). (9) Gayler, Waddle, *J. Am. Chem. Soc.* 63, 3358–3359 (1941). (10) Ipatov, *J. Russ. Phys.-Chem. Soc.* 46, 64 (1914); *Cent.* 1914, I 2161.

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3:8287 *p*-CHLOROTOLUENE $\text{C}_7\text{H}_7\text{Cl}$ 

Beil. V - 292

V<sub>1</sub>-(150)V<sub>2</sub>-(226)

B.P.

M.P.

163.5° cor.	at 764 mm.	{1}	+7.8°	{8}	$D_4^{25} = 1.065$ {16}
162.4°	at 760 mm.	{2}	7.5° {14} {15} {16}		$n_D^{25} = 1.51895$ {9}
		{3}			$D_4^{24.35} = 1.0651$ {21}
162.3°	at 766.4 mm.	{4}	7.4° {17} {4}		$n_D^{24.35} = 1.51925$ {21}
162.0-162.2° cor.		{5}	7.15-7.30° {7}		$D_4^{20} = 1.0700$ {9}
162-163°		{6}	7.1° {18}		1.06974 {17}
161.98-101.99° at 760 mm.		{7}	7° {6} {19}		1.069 {21}
161.7-162.2° cor. at 759.9 mm.		{8}	6.86° {12}		$n_D^{20} = 1.521$ {21}
161.5-161.9° at 760 mm.		{9}	6.85° {20}	See also	
161.0-161.4°		{10}		Note 3.	
160.6-161.2°		{11}	See also Note 2.	$n_D^{19} = 1.5223$ {22}	
162.1° u.c.	at 755 mm.	{12}			

55.57°	at	16 mm. (3)
54.28°	at	15 mm. (3)
52.86°	at	14 mm. (3)
48°	at	12 mm. (13)
45.5°	at	12 mm. (14)
44°	at	10 mm. (15)

$$n_D^{18} = 1.5221 \quad (12)$$

See also Note 4.

See also Note 1.

Note 1. For further data on b.p. of  $\bar{C}$  at 16 pressures from 74–764 mm. see (4).

Note 2. For effect of press. on m.p. see (20).

Note 3. For data on  $D_4^1$  from  $t = 25^\circ$  to  $t = 160^\circ$  see (16) (4); note also  $D_{20}^{20} = 1.0714$  (8).

Note 4. For  $n_D^{19}$ /compn. data on system:  $\bar{C}$  + *o*-chlorotoluene (3:8245) see (22).

$\bar{C}$  with aq. forms a const.-boil. mixt., b.p.  $95^\circ$  (use in sepn. of  $\bar{C}$  from polychlorotoluenes (23)). — For f.p./compn. data on system:  $\bar{C}$  + *o*-chlorotoluene (3:8245) (eutectic, f.p.  $-49.8^\circ$ , contg. 27 wt %  $\bar{C}$ ) see (8) (147); for  $D_{20}^{20}$ /compn. data (8) and for  $n_D^{19}$ /compn. data (22) on this system see indic. refs. — For f.p./compn. data on systems of  $\bar{C}$  with *p*-bromotoluene or with *p*-fluorotoluene see (19). — For data on const.-boil. mixts. of  $\bar{C}$  with various org. cpds. see Beil. V<sub>2</sub>-(227). — For cryoscopic constant (i.e., lowering of f.p. per mole solute per 1000 g  $\bar{C}$ ) viz., 5.53 (12), 5.6 (24), 5.07 (25), see indic. refs.; for use in detn. of  $\bar{C}$  in mixt. with *o*-chlorotoluene (3:8245) and *m*-chlorotoluene (3:8275) see (25).

[For prepn. of  $\bar{C}$  from *p*-toluidine via diazotization in HCl and warming the resultant solution as such (yields: 60% (26), 40–44% (27)) (28) or in pres. of  $Cu_2Cl_2$  (yields: 95% (33), 88–89% (29), 81% (31), 70–79% (30), 63.5% (32)) (for study of kinetics of this reaction see (34) (35)), or in pres. of Cu powder (63.8% yield (36)), or in pres. of CuH (64% yield (37)), or by electrolysis between Cu electrodes in pres. of  $CuCl_2$  (38) see indic. refs.; for prepn. of  $\bar{C}$  from *p*-toluidine via diazotization, conversion to solid *p*-toluenediazonium chloride, and subsequent warming with  $C_6H_6$  +  $AlCl_3$  (39), or via diazotization, conversion of diazonium salt to its cpd. with  $PbCl_4$ , and subsequent htg. of latter in naphthalene at  $150^\circ$  (40), see indic. refs.]

[For formn. of  $\bar{C}$  (usually together with other prods.) from toluene (1:7405) with  $Cl_2$  (70) in pres. of Fe in diffuse light in cold (8) (gives mixt. contg. 42%  $\bar{C}$  + 58% *o*-chlorotoluene (3:8245) (8) (22)), or in pres. of  $I_2$  (22) (41) (42), or in pres. of  $PbCl_2$  (8),  $SbCl_3$  (41),  $MoCl_3$  (43) (28) (44), or  $Al/Hg$  (45); for formn. of  $\bar{C}$  from toluene by electrolysis in strong HCl (46) or in AcOH/conc. HCl in dark (47) see indic. refs.; for formn. of  $\bar{C}$  from toluene with  $SO_2Cl_2$  at  $160^\circ$  (48), with  $SO_2Cl_2$  in pres. of various cat. in dark (49), with  $SO_2Cl_2$  +  $AlCl_3$  +  $S_2Cl_2$  at  $70^\circ$  (50), with pyrosulfuryl chloride +  $AlCl_3$  at  $0^\circ$  (51), with HCl +  $HNO_3$  at  $100^\circ$  (52), with *n*-butyl chlorosulfonate +  $AlCl_3$  (6.2% yield (53)), with anhydrous  $FeCl_3$  after refluxing  $1\frac{1}{2}$  hrs. (65% yield (54)), or with  $NCl_3$  (55) see indic. refs.]

[For formn. of  $\bar{C}$  from *o*-chlorotoluene (3:8245) or *m*-chlorotoluene (3:8275) by partial rearr. with  $AlCl_3$  + HCl gas see (25); from tetra-(*p*-tolyl)tin with  $Cl_2$  in  $CHCl_3$  (85% yield (6)) or from tri-(*p*-tolyl)stibine dichloride on htg. under 5–7 mm. press. at  $60$ – $65^\circ$  (56) (note that at  $160$ – $200^\circ$  di-(*p*-tolyl)stibine chloride is formed (56)) or from tri-(*p*-tolyl)-phosphite dichloride by htg. at  $200$ – $210^\circ$  (57) see indic. refs.; from *p*-tolyl  $MgBr$  in ether with  $Cl_2$  (58) or with benzenesulfonyl chloride (59) see indic. refs.; from *p*-toluenediazopiperidine with conc. HCl see (60); from *p*-chlorobenzaldehyde (3:0765) on elec. reduction in acid soln. with Cu cathode see (61); from chlorobenzene (3:7903) via condensation with  $CH_2O$  + HCl to *p*-chlorobenzyl chloride (3:0220) and subsequent reductn. with  $Zn$  + NaOH see (62)]

[ $\bar{C}$  on pyrolysis over red-hot Pt yields (63) mainly 4,4'-dichlorodihenzyl (1,2-bis-(p-chlorophenyl)ethane [Beil. V-600, V<sub>1</sub>-(281), V<sub>2</sub>-(507)], colorless lfts. from alc., m.p. 112°, accompanied by a very small amt. 4,4'-dichlorostilbene (1,2-bis-(p-chlorophenyl)ethylene) [Beil. V<sub>1</sub>-(304), V<sub>2</sub>-(539)], ndls. from alc., m.p. 170°].

[ $\bar{C}$  with H<sub>2</sub> in pres. of Pd/CaCO<sub>3</sub> (64) or reduced Ni (65) in alc./alk. soln. loses all its halogen as HCl;  $\bar{C}$  with Na in liq. NH<sub>3</sub> as directed (66) yields toluene and other prods.;  $\bar{C}$  with HI + P in s.t. at 302° for 5 hrs. gives (80% yield (67)) toluene.]

$\bar{C}$  on oxidn. with 3 pts. KMnO<sub>4</sub> in dil. aq. soln. under reflux for 4-5 hrs. (68) (51), or with CrO<sub>3</sub> (42), or with dil. HNO<sub>3</sub>, e.g., with 6 pts. of dil. HNO<sub>3</sub> (1 vol. conc. HNO<sub>3</sub> + 2 vols. aq.) at 145° for 1½ hrs. (69) or at 115-120° for 5-6 hrs. (70), yields p-chlorobenzoic acid (3:4940), m.p. 243° (for use in quant. estn. of  $\bar{C}$  in pres. of toluene, benzyl chloride, and o-chlorotoluene see (70)). — Note that with HNO<sub>3</sub>  $\bar{C}$  is more rapidly oxidized than o-chlorotoluene, m-chlorotoluene, or the various dichlorotoluenes but more slowly than p-bromotoluene (69). —  $\bar{C}$  on oxidn. with air at 260° in pres. of Na<sub>2</sub>CO<sub>3</sub> and under press. (71), or on vapor-phase oxidn. over suitable cat. (72), or on electrolytic oxidn. in dil. Na<sub>2</sub>CO<sub>3</sub> soln. at 60° (73) cf. (74), or even on very long atdg. (2 years) with I<sub>2</sub> + aq. in sunlight (75) gives p-chlorobenzoic acid. —  $\bar{C}$  with N<sub>2</sub>O<sub>4</sub> yields (76) p-chlorobenzoic acid accompanied by nitration prods.

[ $\bar{C}$  with chromyl chlorida (CrO<sub>2</sub>Cl<sub>2</sub>) yields an addn. prod. which with aq. gives in good yield (77) p-chlorobenzaldehyde (3:0765). —  $\bar{C}$  with air in aq. susp. of FeO.OH + cat. at 235-240° and 50-60 atm. press. gives (78) a mixt. of p-chlorobenzaldehyde (3:0765) + p-chlorobenzoic acid (3:4940).]

[ $\bar{C}$  with Cl<sub>2</sub> or on htg. with PhCl<sub>2</sub>.2NH<sub>4</sub>Cl or with SO<sub>2</sub>Cl<sub>2</sub> in pres. of dihenzoyl peroxida in dark yields p-chlorobenzyl chloride (3:0220), q.v. for relevant refs. —  $\bar{C}$  with 2 moles Cl<sub>2</sub> in pres. of 5% PCl<sub>5</sub> at 160-170° gives (79) (80) p-chlorobenzal (di)chlorida (3:6700). —  $\bar{C}$  with 3 moles Cl<sub>2</sub> at high temp. in u.v. light (81) cf. (82) or with 3 moles Cl<sub>2</sub> (83) in pres. of FeCl<sub>3</sub> (84) or of PCl<sub>5</sub> (85) (86) gives (93% yield (85)) p-chlorobenzotrichloride (3:6325) q.v. —  $\bar{C}$  with Cl<sub>2</sub> (1 mole) in pres. of 1% Fe or 40% PhCl<sub>2</sub> at 20° gives (65% yield (87)) a mixt. comprising 68.4% 2,4-dichlorotoluene (3:6290) + 41.6% 3,4-dichlorotoluene (3:6355).]

[ $\bar{C}$  with Br<sub>2</sub> at 130° (88) or at 160° (89) (90) or in pres. of dihenzoyl peroxide in dark at 100° (91) gives (21% yield (90)) exclusively (91) p-chlorobenzyl bromide [Beil. V-307, V<sub>2</sub>-(239)], cryst. from MeOH, m.p. 62-63° (88), ndls. from 85% alc., m.p. 50° (90), 51° (79), 48.5° (89); for study of rate of side-chain bromination of  $\bar{C}$  in CS<sub>2</sub> at 57° see (92). —  $\bar{C}$  with 2 moles Br<sub>2</sub> in pres. of BeBr<sub>2</sub> (93) or in AcOH + fumg. HNO<sub>3</sub> + fumg. H<sub>2</sub>SO<sub>4</sub> (94) gives p-chlorobenzal (di)bromide, m.p. 99° (93).]

[ $\bar{C}$  with AlCl<sub>3</sub> + HCl gas as directed (25) undergoes partial rearr. to both o-chlorotoluene (3:8245) and m-chlorotoluene (3:8275); for anal. of mixts. of the three isomers see (25).]

[ $\bar{C}$  with AcCl (95) or better Ac<sub>2</sub>O (96) (97) + AlCl<sub>3</sub> in CS<sub>2</sub> (98) gives (yields: 85% in 4 hrs. (97), 65% (98), 34% in 2 hrs. (96)) 2-chloro-5-methylacetophenone [Beil. VII-307], h.p. 245.8-246.0° at 760.1 mm. (96),  $n_D^{25} = 1.5419$  (96). —  $\bar{C}$  with  $\beta$ -chloropropionyl chloride (3:5690) + AlCl<sub>3</sub> in CS<sub>2</sub> gives (87% yield (99)) (100) 4-chloro-3-( $\beta$ -chloropropionyl)toluene, oil, which on ring closure with conc. H<sub>2</sub>SO<sub>4</sub> gives (72% yield (99)) (100) 7-chloro-4-methylindanone-1, cryst. from MeOH, m.p. 128° (99) (100). —  $\bar{C}$  with trichloroacetonitrile + AlCl<sub>3</sub> (4 moles) at 80-90° satd. with HCl gas for 2 days gives only 6% yield (101) of a mixt. of 2-chloro-5-methyl- and 5-chloro-2-methyl- $\omega,\omega,\omega$ -trichloroacetophenones.]

[ $\bar{C}$  with oxalyl (di)chloride (3:5060) + AlCl<sub>3</sub> in CS<sub>2</sub> for 20 hrs. at room temp. gives (40% yield (102)) 2-chloro-5-methylbenzoic acid (6-chloro-3-methylbenzoic acid) (3:4615), cryst. from aq., m.p. 163-166° (102), accompanied by some dichlorodimethyl-benzophenone, m.p. 70°, whose structure was not detd. —  $\bar{C}$  with fumaryl (di)chloride (3:5875) + AlCl<sub>3</sub>

in  $\text{CS}_2$  at 50–60° for 2 hrs. gives (25% yield (103)) *bis*-1,2-(2-chloro-5-methylbenzoyl)-ethylene, pale yel. cryst. from alc., m.p. 158° (103).]

[ $\bar{\text{C}}$  with benzoyl chloride +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives (50% yield (98)) (104) (105) 2-chloro-5-methylbenzophenone (6-chloro-3-methylbenzophenone) [Beil. VII<sub>1</sub>-(235)], cryst. from  $\text{AcOH}$ , m.p. 35–36° (98) (104) (105), together with 5-chloro-2-methyl-(3-chloro-6-methyl)-benzophenone [Beil. VII<sub>1</sub>-(235)], oil, b.p. 210° at 30 mm. (106). —  $\bar{\text{C}}$  with *o*-chlorobenzoyl chloride (3:6640) +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives (106) 5,2'-dichloro-2-methylbenzophenone [Beil. VII<sub>1</sub>-(235)], oil, b.p. 225° at 12 mm. (106).]

[ $\bar{\text{C}}$  with phthalic anhydride (1:0725) +  $\text{AlCl}_3$  gives (62.5% yield on the phthalic anhydride (107)) *o*-(2-chloro-5-methylbenzoyl)benzoic acid, ndls. from  $\text{C}_6\text{H}_6$ , m.p. 164–165° (107), 165° (108), which with conc.  $\text{H}_2\text{SO}_4$  at 75° for 4 hrs. (108) or with 8 pts. fuming  $\text{H}_2\text{SO}_4$  (20%  $\text{SO}_3$ ) (107) ring-closes to give (yields: 93% (107), 85% (108)) 1-chloro-4-methyl-anthraquinone [Beil. VII-809, VII<sub>1</sub>-(421)], yel. ndls. from  $\text{AcOH}$  or alc., m.p. 164° (107) (108). — Note that the structure of the above keto acid, m.p. 164–165°, has been definitely established (109) as shown and that it is *not* the isomeric *o*-(5-chloro-2-methylbenzoyl)-benzoic acid, which appears to be still unreported. — For reactn. of  $\bar{\text{C}}$  with 3,6-dichlorophthalic anhydride (3:4860) (110) or with pyromellitic anhydride (111) in pres. of  $\text{AlCl}_3$  see indic. refs.]

[ $\bar{\text{C}}$  does *not* (112) react with *bis*-(chloromethyl) ether (3:5245), but  $\bar{\text{C}}$  with formalin + conc.  $\text{HCl}$  yields (62) 4-chloro-3-(chloromethyl)toluene since on reductn. with  $\text{Zn}$  +  $\text{NaOH}$  the prod. gives 4-chloro-1,3-dimethylbenzene (3:8665). —  $\bar{\text{C}}$  with aq. vapor +  $\text{CO}$  over suitable cat. at 300–400° yields (113) *p*-toluic acid (1:0705). —  $\bar{\text{C}}$  with  $\text{NH}_3$  +  $\text{CO}$  over suitable cat. as directed (114) yields *p*-toluidine (see also below). —  $\bar{\text{C}}$  with  $\text{S}_2\text{Cl}_2$  +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives (115) 4,5-dichloro-1,8-dimethylthianthrene, m.p. 195–197° (115).]

[ $\bar{\text{C}}$  with  $\text{Li}$  in ether gives (63% yield (116)) *p*-tolyllithium;  $\bar{\text{C}}$  with  $\text{Li}$  at 150° followed by treatment with aq. gives (117) toluene + 4,4'-dimethylhiphenyl. —  $\bar{\text{C}}$  with  $\text{Na}$  in  $\text{C}_6\text{H}_6$  treated with  $\text{CO}_2$  at ord. temp. (118) (119) or at 50° and 500 lbs. press. (120) cf. (121) gives (yields: 05% (120), 76% (121)) *p*-toluic acid (1:0705), m.p. 178°. —  $\bar{\text{C}}$  with  $\text{Na}$  treated with benzophenone as directed (122) yields diphenyl-*p*-tolyl-carbinol [Beil. VI-722, VI<sub>1</sub>-(355)], m.p. 72–73°.]

[ $\bar{\text{C}}$  on hydrolysis with aq. vapor over silica gel contg. 3% finely divided  $\text{Ni}$  at 380° (123), or with aq. vapor over cat. at 480° (124), or with aq.  $\text{Na}_2\text{CO}_3$  in pres. of  $\text{Cu}$  at 300° under press. (125), or with 15–20% aq.  $\text{NaOH}$  at 300° (126) gives (80% yield (123)) *p*-cresol (1:1410). Note, however, claim (127) that  $\bar{\text{C}}$  when hydrolyzed with 15% aq.  $\text{NaOH}$  in pres. of  $\text{Cu}$  for 2 hrs. at 315–320° yields prod. contg. not only *p*-cresol (1:1410) but also *m*-cresol (1:1730) (for extensive study of hydrolysis of  $\bar{\text{C}}$  as means of prepn. of *m*-cresol see (147)). —  $\bar{\text{C}}$  with  $\text{H}_2\text{S}$  at 700° over suitable cat. yields (128) thio-*p*-cresol (*p*-tolyl-mercaptan).]

[ $\bar{\text{C}}$  with aq.  $\text{NH}_4\text{OH}$  +  $\text{CuO}$  at 150–250° under press. (129) or  $\bar{\text{C}}$  + aq.  $\text{NH}_4\text{OH}$  +  $\text{Cu}$  salts + various anti acids at 225–230° under press. (130) (131) yields *p*-toluidine and/or di-*p*-tolylamine. —  $\bar{\text{C}}$  with  $\text{KNH}_2$  in liq.  $\text{NH}_3$  (132) or  $\text{Na}$  in liq.  $\text{NH}_3$  (66) yields *p*-toluidine. — Note that  $\bar{\text{C}}$  does not react with aq. sodium sulfanilate +  $\text{Na}_2\text{CO}_3$  (dif. from benzyl chloride (3:8535) and use in sepn. of  $\bar{\text{C}}$  from latter (8)).]

[ $\bar{\text{C}}$  on mononitration yields a mixt. contg. both 4-chloro-2-nitrotoluene [Beil. V-327, V<sub>1</sub>-(162), V<sub>2</sub>-(251)], m.p. 38 2° (133), 37–38° (10), 37° (29) (22), b.p. 239 5–240° at 718 mm. (134), 115.5° at 11 mm. (22) (easily volatile with steam, but not reacting with piperidine even after 8 hrs. at 100° (10)), and 4-chloro-3-nitrotoluene [Beil. V-329, V<sub>2</sub>-(252)], m.p. 7° (135), 5 8° (133), b.p. 260° at 745 mm. (135), 118° at 11 mm. (22) (reacts readily with piperidine at 100° (10)); e.g.,  $\bar{\text{C}}$  added in 2 equal portions to 3 wt. pts.  $\text{HNO}_3$  ( $D = 1.5$ ) at 0° gives 88% yield of mixt. contg. 53.8% 4-chloro-2-nitrotoluene + 41.2% 4-chloro-3-



[ $\bar{C}$  on pyrolysis over red-hot Pt yields (63) mainly 4,4'-dichlorodibenzyl (1,2-bis-(p-chlorophenyl)ethane [Beil. V-600, V<sub>1</sub>-(281), V<sub>2</sub>-(507)], colorless lfts. from alc., m.p. 112°, accompanied by a very small amt. 4,4'-dichlorostilbene (1,2-bis-(p-chlorophenyl)ethylene) [Beil. V<sub>1</sub>-(304), V<sub>2</sub>-(539)], ndls. from alc., m.p. 170°.]

[ $\bar{C}$  with H<sub>2</sub> in pres. of Pd/CaCO<sub>3</sub> (64) or reduced Ni (65) in alc./alk. soln. loses all its halogen as HCl;  $\bar{C}$  with Na in liq. NH<sub>3</sub> as directed (66) yields toluene and other prods.;  $\bar{C}$  with HI + P in s.t. at 302° for 5 hrs. gives (80% yield (67)) toluene.]

$\bar{C}$  on oxidn. with 3 pts. KMnO<sub>4</sub> in dil. aq. soln. under reflux for 4-5 hrs. (68) (51), or with CrO<sub>3</sub> (42), or with dil. HNO<sub>3</sub>, e.g., with 6 pts. of dil. HNO<sub>3</sub> (1 vol. conc. HNO<sub>3</sub> + 2 vols. aq.) at 145° for 1½ hrs. (69) or at 115-120° for 5-6 hrs. (70), yields p-chlorobenzoic acid (3:4940), m.p. 243° (for use in quant. estn. of  $\bar{C}$  in pres. of toluene, benzyl chloride, and o-chlorotoluene see (70)). — Note that with HNO<sub>3</sub>  $\bar{C}$  is more rapidly oxidized than o-chlorotoluene, m-chlorotoluene, or the various dichlorotoluenes but more slowly than p-bromotoluene (69). —  $\bar{C}$  on oxidn. with air at 260° in pres. of Na<sub>2</sub>CO<sub>3</sub> and under press. (71), or on vapor-phase oxidn. over suitable cat. (72), or on electrolytic oxidn. in dil. Na<sub>2</sub>CO<sub>3</sub> soln. at 60° (73) cf. (74), or even on very long stdg. (2 years) with I<sub>2</sub> + aq. in sunlight (75) gives p-chlorobenzoic acid. —  $\bar{C}$  with N<sub>2</sub>O<sub>4</sub> yields (76) p-chlorobenzoic acid accompanied by nitration prods.

[ $\bar{C}$  with chromyl chloride (CrO<sub>2</sub>Cl<sub>2</sub>) yields an addn. prod. which with aq. gives in good yield (77) p-chlorobenzaldehyde (3:0765). —  $\bar{C}$  with air in aq. susp. of FeO.OH + cat. at 235-240° and 50-60 ntm. press. gives (78) a mixt. of p-chlorobenzaldehyde (3:0765) + p-chlorobenzoic acid (3:4940).]

[ $\bar{C}$  with Cl<sub>2</sub> or on htg with PbCl<sub>4</sub>·2NH<sub>4</sub>Cl or with SO<sub>2</sub>Cl<sub>2</sub> in pres. of dibenzoyl peroxide in dark yields p-chlorobenzyl chloride (3:0220), q.v. for relevant refs. —  $\bar{C}$  with 2 moles Cl<sub>2</sub> in pres. of 5% PCl<sub>5</sub> at 160-170° gives (79) (80) p-chlorobenzal (di)chloride (3:6700). —  $\bar{C}$  with 3 moles Cl<sub>2</sub> at high temp. in u.v. light (81) cf. (82) or with 3 moles Cl<sub>2</sub> (83) in pres. of FeCl<sub>3</sub> (84) or of PCl<sub>5</sub> (85) (86) gives (93% yield (85)) p-chlorobenzotrichloride (3:6825) q.v. —  $\bar{C}$  with Cl<sub>2</sub> (1 mole) in pres. of 1% Fe or 40% PbCl<sub>2</sub> at 20° gives (65% yield (87)) a mixt. comprising 58.4% 2,4-dichlorotoluene (3:6290) + 41.6% 3,4-dichlorotoluene (3:6355).]

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[ $\bar{C}$  with AcCl (95) or better Ac<sub>2</sub>O (96) (97) + AlCl<sub>3</sub> in CS<sub>2</sub> (98) gives (yields: 85% in 4 hrs. (97), 65% (98), 34% in 2 hrs. (96)) 2-chloro-5-methylacetophenone [Beil. VII-307], b.p. 245.8-246.0° at 760.1 mm. (96),  $n_D^{25}$  = 1.5419 (96). —  $\bar{C}$  with  $\beta$ -chloropropionyl chloride (3:5690) + AlCl<sub>3</sub> in CS<sub>2</sub> gives (87% yield (99)) (100) 4-chloro-3-( $\beta$ -chloropropionyl)toluene, oil, which on ring closure with conc. H<sub>2</sub>SO<sub>4</sub> gives (72% yield (99)) (100) 7-chloro-4-methylindanone-1, cryst. from MeOH, m.p. 128° (99) (100). —  $\bar{C}$  with trichloroacetoneitrile + AlCl<sub>3</sub> (4 moles) at 80-90° satd. with HCl gas for 2 days gives only 5% yield (101) of a mixt. of 2-chloro-5-methyl- and 5-chloro-2-methyl- $\omega,\omega,\omega$ -trichloroacetophenones.]

[ $\bar{C}$  with oxalyl (di)chloride (3:5060) + AlCl<sub>3</sub> in CS<sub>2</sub> for 20 hrs. at room temp. gives (40% yield (102)) 2-chloro-5-methylbenzoic acid (6-chloro-3-methylbenzoic acid) (3:4615), cryst. from aq., m.p. 163-166° (102), accompanied by some dichlorodimethyl-benzophenone, m.p. 70°, whose structure was not detd. —  $\bar{C}$  with fumaryl (di)chloride (3:5875) + AlCl<sub>3</sub>

in  $\text{CS}_2$  at 50–60° for 2 hrs. gives (25% yield {103}) bis-1,2-(2-chloro-5-methylbenzoyl)-ethylene, pale yel. cryst. from alc., m.p. 158° {103}.

[ $\bar{\text{C}}$  with benzoyl chloride +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives (50% yield {98}) {104} {105} 2-chloro-5-methylbenzophenone (6-chloro-3-methylbenzophenone) [Beil. VII-235], cryst. from  $\text{AcOH}$ , m.p. 35–36° {98} {104} {105}, together with 5-chloro-2-methyl-(3-chloro-6-methyl)-benzophenone [Beil. VII-235], oil, b.p. 210° at 30 mm. {106}. —  $\bar{\text{C}}$  with *o*-chlorobenzoyl chloride (3:6640) +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives {106} 5,2'-dichloro-2-methylbenzophenone [Beil. VII-235], oil, h.p. 225° at 12 mm. {106}.]

[ $\bar{\text{C}}$  with phthalic anhydride (1:0725) +  $\text{AlCl}_3$  gives (62.5% yield on the phthalic anhydride {107}) *o*-(2-chloro-5-methylbenzoyl)benzoic acid, ndls. from  $\text{C}_6\text{H}_6$ , m.p. 164–165° {107}, 165° {108}, which with conc.  $\text{H}_2\text{SO}_4$  at 75° for 4 hrs. {108} or with 8 pts. fuming  $\text{H}_2\text{SO}_4$  (20%  $\text{SO}_3$ ) {107} ring-closes to give (yields: 93% {107}, 85% {108}) 1-chloro-4-methyl-anthraquinone [Beil. VII-809, VII-421], yel. ndls. from  $\text{AcOH}$  or alc., m.p. 164° {107} {108}. — Note that the structure of the above keto acid, m.p. 164–165°, has been definitely established {109} as shown and that it is *not* the isomeric *o*-(5-chloro-2-methylbenzoyl)-benzoic acid, which appears to be still unreported. — For reactn. of  $\bar{\text{C}}$  with 3,6-dichlorophthalic anhydride (3:4860) {110} or with pyromellitic anhydride {111} in pres. of  $\text{AlCl}_3$  see indic. refs.]

[ $\bar{\text{C}}$  does *not* {112} react with bis-(chloromethyl) ether (3:5245), but  $\bar{\text{C}}$  with formalin + conc.  $\text{HCl}$  yields {62} 4-chloro-3-(chloromethyl)toluene since on reductn. with  $\text{Zn}$  +  $\text{NaOH}$  the prod. gives 4-chloro-1,3-dimethylbenzene (3:8665). —  $\bar{\text{C}}$  with aq. vapor +  $\text{CO}$  over suitable cat. at 300–400° yields {113} *p*-toluic acid (1:0795). —  $\bar{\text{C}}$  with  $\text{NH}_3$  +  $\text{CO}$  over suitable cat. as directed {114} yields *p*-toluidine (see also below). —  $\bar{\text{C}}$  with  $\text{S}_2\text{Cl}_2$  +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives {115} 4,5-dichloro-1,8-dimethylthianthrene, m.p. 195–197° {115}.]

[ $\bar{\text{C}}$  with  $\text{Li}$  in ether gives (63% yield {116}) *p*-tolyllithium;  $\bar{\text{C}}$  with  $\text{Li}$  at 150° followed by treatment with aq. gives {117} toluene + 4,4'-dimethylbiphenyl. —  $\bar{\text{C}}$  with  $\text{Na}$  in  $\text{C}_6\text{H}_6$  treated with  $\text{CO}_2$  at ord. temp. {118} {119} or at 50° and 500 lbs. press. {120} cf. {121} gives (yields: 95% {120}, 76% {121}) *p*-toluic acid (1:0795), m.p. 178°. —  $\bar{\text{C}}$  with  $\text{Na}$  treated with benzophenone as directed {122} yields diphenyl-*p*-tolyl-carbinol [Beil. VI-722, VI-355], m.p. 72–73°.]

[ $\bar{\text{C}}$  on hydrolysis with aq. vapor over silica gel contg. 3% finely divided  $\text{Ni}$  at 380° {123}, or with aq. vapor over cat. at 480° {124}, or with aq.  $\text{Na}_2\text{CO}_3$  in pres. of  $\text{Cu}$  at 300° under press. {125}, or with 15–20% aq.  $\text{NaOH}$  at 300° {126} gives (80% yield {123}) *p*-cresol (1:1410). Note, however, claim {127} that  $\bar{\text{C}}$  when hydrolyzed with 15% aq.  $\text{NaOH}$  in pres. of  $\text{Cu}$  for 2 hrs. at 315–320° yields prod. contg. not only *p*-cresol (1:1410) but also *m*-cresol (1:1730) (for extensive study of hydrolysis of  $\bar{\text{C}}$  as means of prepn. of *m*-cresol see {147}). —  $\bar{\text{C}}$  with  $\text{H}_2\text{S}$  at 700° over suitable cat. yields {128} thio-*p*-cresol (*p*-tolyl-mercaptan).]

[ $\bar{\text{C}}$  with aq.  $\text{NH}_4\text{OH}$  +  $\text{CuO}$  at 150–250° under press. {129} or  $\bar{\text{C}}$  + aq.  $\text{NH}_4\text{OH}$  +  $\text{Cu}$  salts + various anti acids at 225–230° under press. {130} {131} yields *p*-toluidine and/or di-*p*-tolylamine. —  $\bar{\text{C}}$  with  $\text{KNH}_2$  in liq.  $\text{NH}_3$  {132} or  $\text{Na}$  in liq.  $\text{NH}_3$  {66} yields *p*-toluidine. — Note that  $\bar{\text{C}}$  does not react with aq. sodium sulfanilate +  $\text{Na}_2\text{CO}_3$  (dif. from benzyl chloride (3:8535) and use in sepn. of  $\bar{\text{C}}$  from latter {8}).]

[ $\bar{\text{C}}$  on mononitration yields a mixt. contg. both 4-chloro-2-nitrotoluene [Beil. V-327, V-162],  $V_2$ -251], m.p. 38.2° {133}, 37–38° {10}, 37° {29} {22}, h.p. 239.5–240° at 718 mm. {134}, 115.5° at 11 mm. {22} (easily volatile with steam, but not reacting with piperidine even after 8 hrs. at 100° {10}), and 4-chloro-3-nitrotoluene [Beil. V-329,  $V_2$ -252], m.p. 7° {135}, 5.8° {133}, b.p. 260° at 745 mm. {135}, 118° at 11 mm. {22} (reacts readily with piperidine at 100° {10}); e.g.,  $\bar{\text{C}}$  added in 2 equal portions to 3 wt. pts.  $\text{HNO}_3$  ( $D = 1.5$ ) at 0° gives 88% yield of mixt. contg. 58.8% 4-chloro-2-nitrotoluene + 41.2% 4-chloro-3-





760-762, 772-773 (1898). (143) Vogt, Henninger, *Ann.* **165**, 363-365 (1873). (144) DeRoode,  
*Am. Chem.* **17**, 925 (1901). (145) W.-L. Ditt, *Ber.* **180**, 927 (1901).  
S., 1921; S  
Huntress,  
38, 254-261 (1946).

3:8290 ETHYL  $\beta$ -CHLOROPROPIONATE

Beil. II - 250

 $\Pi_1 - (111)$ 

Π<sub>2</sub>-(227)

B.P. 162-163° at 765 mm. (1)

$$D_i^{20} = 1.1086 \quad (5) \quad D_0^{20} = 1.42537 \quad (5)$$

**162.5°** at 761 mm. (2)

1.1025 (18)	1.4269 (18)
-------------	-------------

162-163° at 760 mm. (3)

**162<sup>a</sup>** (4)

$$D_1^{15} = 1.1141 \quad (2) \quad n_D^{15} = 1.4284 \quad (2)$$

161.4–161.8° at 758 mm. (5)

161<sup>a</sup> (6)80<sup>a</sup> at 29 mm. (2)

61.5° at 15 mm. (7)

[For prepn. of  $\bar{C}$  from  $\beta$ -chloropropionic acid (3:0460) by esterification with EtOH + HCl (59% yield (6)) (4) or  $H_2SO_4$  (1) see indicated refs.; from  $\beta$ -chloropropionyl chloride (3:5690) + EtOH see (1); from acrylic acid chloride (3:7153) + EtOH see (4) (7); from ethyl acrylate (1:3071) + HCl see (2); from acrylonitrile + HCl to  $\beta$ -chloropropionitrile followed by reactn. with EtOH see (8); from ethyl lactate (1:3303) +  $SOCl_2$  + pyridine (95% yield (9)) see (9).]

(11) gives (90% yield (10)) ethyl acrylate (1:3071), b.p. 101°.

On reflux with NaI in acetone gives (yield: 81% (12), 75-80% (13)) ethyl  $\beta$ -iodopropionate, b.p. 183-185° at 760 mm. (13). [For study of rate of reactn. with KI in acetone see (6).] [Note also that  $\beta$ -iodopropionic acid with alc. HCl (as in its esterification) gives some ethyl  $\beta$ -chloropropionate (14).]

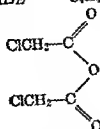
On catalytic hydrogenation as specified (7) takes up only a little  $H_2$  [dif. from ethyl  $\alpha$ -chloropropionate which gives quant. ethyl propionate].

[For reacts. of  $\bar{C}$  with  $CH_3MgI$  (15),  $C_2H_5MgBr$  (16), and other  $RMgX$  cpds. (17) see indicated refs.]

1931, II 2658. (9) Darzen, *Compt. rend.* **152**, 1601 (1911). (10) Hohn, Haas, Ger. 546,141, March 12, 1932; *Cent.* 1932, I 2642.

(11) Brit. 351,518, July 23, 1931; *Cent.* 1931, II 1923. (12) Baker, *J. Chem. Soc.* 1933, 216. (13) Borsche, *Ann.* 526, 16 (1936). (14) Flörsheim, *J. prakt. Chem.* (2) 68, 346 (1903). (15) Bennett, Philip, *J. Chem. Soc.* 1928, 1937-1942. (16) Moureu, Barrett, *Bull. soc. chim.* (4) 29, 994-996 (1921). (17) Weizmann, Bergmann, *J. Chem. Soc.* 1936, 401-402. (18) Schjånberg, *Z. physik. Chem. A* 172, 231 (1935).

## 3:0730 CHLOROACETIC ACID ANHYDRIDE


 Beil. II - 199  
 II<sub>1</sub> - (89)  
 II<sub>7</sub> - (193)


M.P. 48-49° (16)	B.P. 163°	at 116 mm. (4)	$D_4^{50} = 1.3604$ (5)
46-47° (1)	161°	at 104 mm. (4)	$D_4^{20} = 1.5497$ (5)
46° (2)	149°	at 62 mm. (4)	
45.2° (3)	144°	at 51 mm. (4)	
	135°	at 36 mm. (4)	
	126-128°	at 30 mm. (5)	
	126°	at 24 mm. (4)	
	115-120°	at 20 mm. (6)	
	109-110°	at 10 mm. (2)	
	108-110°	at 10 mm. (16)	

Note that the above name of  $\bar{C}$  is so rendered to emphasize that it is the anhydride of chloroacetic acid (not a monochlorinated acetic anhydride).

Fr. from  $\text{C}_2\text{H}_5$ ; eas. sol. cold ether,  $\text{CHCl}_3$ ; spar. sol. cold  $\text{C}_6\text{H}_6$ ; insol. cold lgr.

[For prepn of  $\bar{C}$  from chloroacetic acid (3:1370) with  $\text{P}_2\text{O}_5$  in vac. (2), or with  $\text{Ac}_2\text{O}$  (5) (6) (in latter case note also formn. of mixed anhydride acetic-chloroacetic anhydride, b.p. 80-83° at 30 mm. (5), 80-85° at 20 mm. (3),  $D_4^{20} = 1.2003$  (5)), or with chloroacetyl chloride (3:5235) + an inorg acid chloride (7) or  $\text{AlCl}_3$  (8), see indic. refs.; for prepn. of  $\bar{C}$  from sodium chloroacetate with oxalyl (di)chloride (3:5060) in  $\text{C}_6\text{H}_6$  (54% yield) see (9); for prepn. of  $\bar{C}$  from chloroacetyl chloride (3:5235) with  $\text{Na}_2\text{CO}_3$  (4) or  $\text{KNO}_3$  (1) see indic. refs.]

$\bar{C}$  with aq  $\text{K}_2\text{CO}_3$  yields (2) polyglycolide (1:4976), m.p. 220°.

[For reactn. of  $\bar{C}$  with  $\text{AlCl}_3$  + toluene giving 46-59%  $\omega$ -chloro-*p*-methylacetophenone (3:1130) see (10); for reactn. of  $\bar{C}$  with  $\text{AlCl}_3$  + biphenyl giving 41% yield  $\omega$ -chloro-*p*-phenylacetophenone, pale yel ndls. from dil. alc, m.p. 122-123° see (11); for abnormal reactn. of  $\bar{C}$  with benzyl  $\text{MgCl}$  yielding  $\omega$ -chloro-*o*-methylacetophenone (3:9660) see (12).]

[For behavior of  $\bar{C}$  with various carbohydrates (13) and with cellulose (14) see indic. refs.]

$\bar{C}$  htd. 4 hrs. at 160-180° with phenyl isothiocyanate yields (15) after distn. at 14-20 mm. 2,4-dioxo-3-phenylthiazolidine [Beil. XXVII-238, XXVII<sub>1</sub>-(305)], m.p. 147-148° (15).]

$\bar{C}$  with aq hydrolyzes almost instantly yielding chloroacetic acid (3:1370). — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see chloroacetic acid (3:1370).

3:0730 (1) Diels, Okada, *Ber.* 44, 3335 (1911). (2) Bischoff, Walden, *Ber.* 27, 2949 (1894). (3) Watson, Gregory, *J. Chem. Soc.* 1929, 1375. (4) Patterson, *Ber.* 33, 219-213 (1905). (5) Baroni, *Gazz. chim. ital.* 63, 29-30 (1933). (6) Clarke, Malm (to Eastman Kodak Co.), U.S. 1,618,540, Nov. 8, 1927; *Cent.* 1928, I 1459; *C.A.* 22, 423 (1928). (7) Salmoiraghi, *Italian* 290,541, June 17, 1930, *Cent.* 1937, I 185. (8) Strosacker, Schwegler (to Dow Chem. Co.), U.S. 1,713,101, May 14, 1929, *Cent.* 1929, II 1215; *C.A.* 23, 3234-3235 (1929). (9) Adams, Ulich, *J. Am. Chem. Soc.* 42, 607 (1920). (10) Noller, Adams, *J. Am. Chem. Soc.* 46, 1892-1893 (1921).

(11) Silver, Lowy, *J. Am. Chem. Soc.* 56, 2429-2430 (1934). (12) Austin, Johnson, *J. Am. Chem. Soc.* 54, 656 (1932). (13) Brass, Kurz, *Cellulosechem.* 15, 99-102 (1934). (14) Soc. Chem. Ind. Basel, French 764,308, May 18, 1934; *Cent.* 1935, I 650. (15) Dabeky, *Ber.* 50, 1690-1691 (1917). (16) Ballaus, *Monatsh.* 74, 91 (1943).

3:8307 ETHYL *d,l*- $\alpha$ -CHLORO-*n*-BUTYRATE  $C_6H_{11}O_2Cl$  Beil. II-277  
 $CH_3.CH_2.CH.COOC_2H_5$  II<sub>1</sub>—  
 $\quad \quad \quad |$  II<sub>2</sub>—  
 $\quad \quad \quad Cl$

B.P. 163-164° at 760 mm. (1)  $D_4^{13} = 1.056$  (1)  $n_D^{20} = 1.42430$  (1)  
 156-160° (2)

$D_4^{17.5} = 1.063$  (2)

[For prepn. of  $\bar{C}$  from  $\alpha$ -chloro-*n*-butyronitrile with EtOH (2) or with EtOH + HCl (1) see indic. refs.; for formn. of  $\bar{C}$  from ethyl *n*-butyrate (1:3127) with  $SO_2Cl_2$  + dibenzoyl peroxide in  $CCl_4$  (10%  $\bar{C}$  + 50%  $\beta$ - and 40%  $\gamma$ -isomers (3)) see (3).]

[For use of  $\bar{C}$  in Reformatsky reactn. see (4).]

For the amide corresp. to  $\bar{C}$  see  $\alpha$ -chloro-*n*-butyric acid (3:9130).

3:8307 (1) Henry, *Bull. acad. roy. Belg.* (3) 35, 507-520 (1898); *Cent.* 1898, I 273. (2) Markownikow, *Ann.* 153, 241 (1870). (3) Price, Schwarz, *J. Am. Chem. Soc.* 62, 2864-2895 (1940). (4) Nieuwland, Daly, *J. Am. Chem. Soc.* 53, 1842-1846 (1931).

3:8310  $\gamma$ -CHLORO-*n*-PROPYL ACETATE  $C_6H_9O_2Cl$  Beil. II —  
 (1-Acetoxy-3-chloropropane;  $ClCH_2.CH_2.CH_2.O.CO.CH_3$  II<sub>1</sub>-( 58)  
 trimethylene chlorohydrin acetate) VI - 1281  
 II<sub>2</sub>-( 139)

B.P. 165-166° (1)  $D_4^{21} = 1.1105$  (7)  $n_D^{21} = 1.431$  (7)  
 168-173° (2)  
 163-165° at 747 mm. (3)  
 160-166° (4)  
 88-90° at 22 mm. (5)  
 66° at 14 mm. (6)  
 62-63° at 10 mm. (7)

Beil. II - 198

Π<sub>1</sub>-( 89)

И?  
И?  
И?

—

$$D_4^{20} = 1.1033(6) \quad n_D^{20} = 1.4261(6)$$

1.1050 (2)	1.4256 (2)
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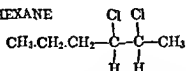
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161<sup>a</sup> at 740 mm. (5)

3:8295 (1) Cheng, Z. *physik. Chem.* B-24, 307 (1934). (2) Drushel, Hill, *Am. J. Sci.* (4) 30, 72-78 (1910); *C.A.* 4, 2438 (1910). (3) Schiff, Z. *physik. Chem.* 1, 378 (1887). (4) Henry, *Compt. rend.* 100, 115 (1885). (5) Schreiner, *Ann.* 197, 8 (1879). (6) Schjaneberg, Z. *physik. Chem.* A-172, 228 (1935).

$$\text{C}_6\text{H}_{12}\text{Cl}_2$$

Beil. 1 - 144



I—

**I<sub>2</sub>-(100)**

B.P. 162-165° (1)

$$D_{11}^{11} = 1.0527(1)$$

[For prepn. of  $\bar{C}$  from 2,3-epoxyhexane with  $PCl_5$  see (1) (2).]

is not attacked by solid KOH but with alc. KOH yields (1) as chlorohexane, b.p. 122° (1).

3:8300 (1) Henry, *Bull. soc. chim.* (2) 41, 363 (1884). (2) Henry, *Compt. rend.* 97, 262 (1883).

$$\text{C}_7\text{H}_{13}\text{OCl}$$

Bell. II —

(*sec.*-Amyl-(2)-acetyl chloride)

$$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}$$

И, —

II<sub>2</sub>-(298)

1

B.P. 163-164° at 751 mm. (1)

$$D_4^{70} = 0.987 \text{ (1)}$$

159-161° at 733 mm. (2)

[For prepn. of **5** from methyl-*n*-propyl-acetic acid (Beil. II<sub>1</sub>-(146)) (1) (2) with PCl<sub>3</sub> (1) or SOCl<sub>2</sub> (87% yield (2)) see indic. refs.]

[C with *n*-propyl zinc iodide in toluene gives (70% yield (2)) 6-methylnonanone-4, b.p. 192–193° at 715 mm. (2).]

On hydrolysis yields (1)  $\beta$ -methyl-*n*-caproic acid, [Bcil. II<sub>1</sub>-(146)] (1) (2), b.p. 215–216° (3), 212–213° at 755 mm. (1), 207–209° u.c. at 723 mm. (2).

Ⓐ *β*-Methyl-*n*-caproamide: m.p. 97° (1), 99° (4). [From **C** + excess conc. aq.  $\text{NH}_4\text{OH}$  (1)]

3:8365 (1) Dewael, Weckering, *Bull. soc. chim. Belg.* 33, 496-497 (1924). (2) Karrer, Shibata, Wettstein, Jacobowicz, *Helv. Chim. Acta* 13, 1302-1303 (1930). (3) Ciarnician, Silber, *Ber.* 46, 3080 (1913). (4) Bayer & Co., *Ger.* 228,667, Nov. 15, 1910; *Cent.* 1910, II 1789.



$D_4^{20} = 1.0884$ ,  $n_D^{20} = 1.4579$  (9); cf. behavior of stereoisomeric ethyl  $\beta$ -chlorocrotonate (3:8538).]

$\bar{C}$  with hydrazine hydrate in abs. alc. splits out HCl and EtOH with consequent ring closure yielding (18) 5-methylpyrazolone-3 [Beil. XXIV-19, XXIV<sub>1</sub>-(189)], m.p. 215° (18); note that same prod. is also obtd. from methyl  $\beta$ -chloroisocrotonate (3:8028).

$\bar{C}$  (1 mole) with phenylhydrazine (1 mole) at 100° for 6-8 hrs. gives by ring closure mainly (4) 3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-20, XXIV<sub>1</sub>-(190)], pr. from aq., m.p. 127°, accompanied by small amts. of 4-benzeneazo-3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-328, XXIV<sub>1</sub>-(319)], m.p. 155-156°, and 3,3'-dimethyl-1,1'-diphenyl-bis pyrazolone-5,5' [Beil. XXVI-484], dec. at high temp. without melting. — Note that with excess phenylhydrazine (2-4 moles) only traces of the 3-methyl-1-phenylpyrazolone-5 are formed while the amt. of the other two (less desirable) prods. is greatly increased (4).

3:8325 (1) Kohlrausch, Pongratz, *Z. physik. Chem.* 27, 193 (1934). (2) Geuther, Frölich, *Zeit. für Chemie* 1869, 273. (3) Eisenlohr, *Ber.* 44, 3208 (1911). (4) Autenrieth, *Ber.* 29, 1654-1664 (1896). (5) Koll, *Ann.* 249, 323-324 (1888). (6) Lauer, Kilburn, *J. Am. Chem. Soc.* 59, 2587 (1937). (7) von Auwers, *Ber.* 56, 724 (1923). (8) von Auwers, *Ber.* 45, 2807-2808 (1912). (9) Gidvani, Kon, Wright, *J. Chem. Soc.* 1932, 1034-1035. (10) Errera, Lepingle, *Bull. sci. acad. roy. Belg.* (5) 11, 150-153 (1925); *Cent.* 1925, II 897; *C.A.* 19, 3057 (1925).

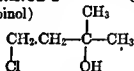
(11) von Auwers, *Ann.* 432, 62 (1923). (12) Scheibler, Voss, *Ber.* 53, 381-382, 387-388 (1920). (13) Thomas-Mamert, *Bull. soc. chim.* (3) 13, 70-71 (1895). (14) Scheibler, Bube, *Ber.* 48, 1449-1451 (1915). (15) Scheibler, Topouzada, Schulze, *J. prakt. Chem.* (2) 124, 7-12 (1930). (16) Ruhemann, Wragg, *J. Chem. Soc.* 79, 1190 (1901). (17) Fichter, Schwab, *Ann.* 348, 251-256 (1906). (18) Freri, *Gazz. chim. ital.* 66, 25 (1936); *Cent.* 1936, II 621; *C.A.* 30, 6387 (1936).

### 3:8335 4-CHLORO-2-METHYLBUTANOL-2

( $\beta$ -Chloroethyl-dimethyl-carbinol)

$C_6H_{11}OCl$

Beil. I - 390



I<sub>1</sub>—  
I<sub>2</sub>-(424)

B.P. 166° (1)

72° at 13 mm. (2)

62-63° at 14 mm. (3)

[For prepn. of  $\bar{C}$  from methyl  $\beta$ -chloropropionate (3:5765) (3) or from ethyl  $\beta$ -chloropropionate (3:8290) (1) (53% yield (2)) with MeMgBr see indic. refs.]

$\bar{C}$  with fuming HCl at room temp. yields (1) 2,4-dichloro-2-methylbutane (3:8105).

$\bar{C}$  mixed with 3 pts. dry powdered KOH and htd. at 130-180° gives (43% yield (2)) by loss of HCl and ring closure 2,4-epoxy-2-methylbutane ( $\alpha,\alpha$ -dimethyltrimethylene oxide), b.p. 71° at 750 mm.,  $D_4^{20} = 0.8279$  (2).

$\bar{C}$  with specially dried K phthalimide htd. in a s.t. 8 hrs. at 169°, finally 3½ hrs. at 218°, yields (3) (by metathesis and loss of H<sub>2</sub>O) *N*-(2-methylbuten-2-yl-4)phthalimide, m.p. 99° (3).

3:8335 (1) Henry, *Bull. soc. chim. Belg.* 20, 152-156 (1906); *Cent.* 1906, II 1178; *Compt. rend.* 142, 133 (1906). (2) Bennett, Philip, *J. Chem. Soc.* 1928, 1938. (3) Späth, Spitzky, *Ber.* 59, 2276-2277 (1925).

3:8325 ETHYL  $\beta$ -CHLOROISOCROTONATE

Beil. II - 417

 $\Pi_1$ -(190) $\Pi_2$ -(397)

B.P.	B.P. (contd)			
165.6-167.2°	(1)	60° at 15 mm.	(7)	$D_4^{20} = 1.088$ (8)
164°	(13)	56-57° at 13 mm.	(8) (9)	1.087 (7)
161.4°	(2)	54° at 14 mm.	(10)	1.086 (11)
159-161°	(3)	50° at 10 mm.	(11)	$n_D^{20} = 1.4538$ (7)
157-158° at 740 mm.	(4)			$D_4^{18.7} = 1.0924$ (3)
155-156°	(5)			$n_D^{18.7} = 1.45423$ (3)
154-157°	(6)			$D_4^{17.7} = 1.0896$ (8)
				$n_D^{17.7} = 1.45467$ (8)
				$D_4^{14.4} = 1.0920$ (11)

[See also ethyl  $\beta$ -chlorocrotonate (3:8538).]

Note the lack of accord regarding the b.p. of  $\bar{C}$  especially at ordinary pressures; this is presumably attributable to more or less contamination with the stereoisomeric ester (3:8538).

[For prepn. of  $\bar{C}$  from  $\beta$ -chloroisocrotonic acid (3:1300) in EtOH with dry HCl gas (yields: 100% (4), 65% (12)) (2) (5) or a little conc.  $\text{H}_2\text{SO}_4$  (yield 65% (6)) (8) (11) see indic. refs.]

[For prepn. of  $\bar{C}$  from ethyl acetoacetate (1:1710) with  $\text{PCl}_5$  in  $\text{C}_6\text{H}_6$  followed by refluxing with a little  $\text{I}_2$  see (13) (1); note, however, that this method has subsequently (6) been regarded as unsatisfactory for the prepn. of pure  $\bar{C}$  although it suffices to give (40-50% yields (14)) a mixt. of  $\bar{C}$  with its stereoisomer (3:8538) which for many purposes is adequate.]

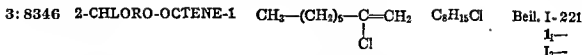
[ $\bar{C}$  (2 moles) with  $\text{K}_2\text{S}$  ( $1\frac{1}{2}$  moles) in 5 vols. abs. EtOH refluxed for 5 hrs. (note that the stereoisomer (3:8538) requires 16) gives (53% yield (14)) diethyl  $\beta, \beta'$ -thiodicrotonate,  $\text{S}(-\text{C}(\text{CH}_3)=\text{CH}.\text{COOC}_2\text{H}_5)_2$ , h.p. 150-153° at 4 mm. (14), accompanied by some ethyl  $\beta$ -mercaptocrotonate (see below).]

[ $\bar{C}$  with alc. NaSH as directed gives (55-60% yield crude prod. (15)) ethyl  $\beta$ -mercaptocrotonate, note that this prod. is apparently a mixt. of the two geom. stereoisomeric thioenols together with the keto form, viz., ethyl thioacetoacetate,  $\text{CH}_3\text{CS}.\text{CH}_2.\text{COOC}_2\text{H}_5$ ; for details see (15); note also that ethyl  $\beta$ -chlorocrotonate (3:8538) by the same treatment gives the same result so that a mixt. of the esters can be employed as initial material.]

[ $\bar{C}$  with alkali derivs. of alcohols, phenols, mercaptans, etc., splits out alkali halide yielding corresp. ethyl  $\beta$ -substituted crotonates: e.g.,  $\bar{C}$  with NaOEt in ether gives (5) ethyl  $\beta$ -ethoxycrotonate [Beil. III-373, III<sub>1</sub>-(135), III<sub>2</sub>-(254)], m.p. 29.5° (5);  $\bar{C}$  with Na allylate gives (6) ethyl  $\beta$ -allyloxycrotonate;  $\bar{C}$  with Na cinnamylate gives (6) ethyl  $\beta$ -cinnamylloxycrotonate;  $\bar{C}$  with Na phenolate gives (16) ethyl  $\beta$ -phenoxyacrylate, h.p. 152° at 18 mm. (16); note that in the three preceding cases either  $\bar{C}$  or its stereoisomer (3:8538) yields the same result.]

[ $\bar{C}$  with Na salt of ethyl mercaptan gives (12) ethyl  $\beta$ -ethylmercaptacisocrotonate, h.p. 127-129° at 16 mm. (12);  $\bar{C}$  with Na salt of benzyl mercaptan gives (75% yield (12)) a mixt. of ethyl  $\beta$ -benzylmercaptocrotonate, m.p. 64.5° (12), and ethyl  $\beta$ -benzylmercaptacisocrotonate (const. not given).]

[ $\bar{C}$  with diethyl sodiomalonate gives (9) cf. (17) *cis* diethyl  $\alpha$ -carbethoxy- $\beta$ -methylglutamate,  $(\text{C}_2\text{H}_5\text{OOC})_2\text{CH}.\text{C}(\text{CH}_3)=\text{CH}.\text{COOC}_2\text{H}_5$  [Beil. II-553], h.p. 164-165° at 12 mm.,



B.P. 168-170° (1)

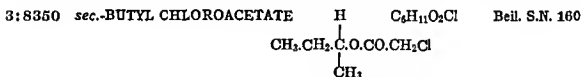
 $D_4^0 = 0.0274$  (2)

167-168° (2)

[For prepn. of  $\bar{\text{C}}$  from ( $\beta$ -chloro- $\beta$ -n-bethylvinyl)arsonic acid by htg. at 175° (1) or from octanone-2 (1:5490) with  $\text{PCl}_5$  (2) see indic. refs.]

[Note that the structure of  $\bar{\text{C}}$  has not been unequivocally demonstrated, and it may be 2-chloro-octene-2 (3:8345).]

3:8346 (1) Fusco, Cottignoli, *Farm. ital.* 11, 89-91 (1943); *Cent.* 1943, II 2285; *C.A.* 38, 6054 (1944). (2) Béhal, *Ann. chim.* (6) 15, 277-278 (1888).



B.P. 167.5° at 760 mm. (2)

 $D_{20}^{20} = 1.062$  (2)  $n_D^{19} = 1.4251$  (1)

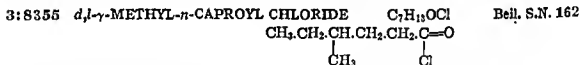
163-164° (1)

 $D_{15}^{15} = 1.055$  (1)

[For prepn. from butene-2 + chloroacetic ac. (3:1370) +  $\text{ZnCl}_2$  see (1).]

[For study of insecticidal action of vapor of  $\bar{\text{C}}$  see (2).]

3:8350 (1) Aldoschin, *J. Gen. Chem. (U.S.S.R.)* 8, 1385-1389 (1938); *Cent.* 1939, II 2223; *C.A.* 33, 4194 (1939). (2) Roark, Cotton, *Ind. Eng. Chem.* 29, 512-514 (1928).



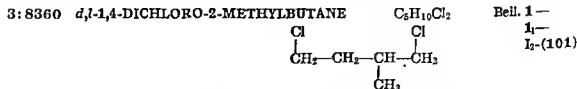
B.P. 167-168° at 767 mm. (1)

 $D_4^{20} = 0.0677$  (1)

[For prepn. of  $\bar{\text{C}}$  from  $\gamma$ -methyl-*n*-caproic acid (1:1136) with  $\text{PCl}_3$  see (1).] [The dextrorotatory isomer of  $\bar{\text{C}}$ , b.p. 80° at 50 mm. (2), has been prepared from the dextrorotatory acid +  $\text{SOCl}_2$ .]

$\bar{\text{C}}$  on hydrolysis yields  $\gamma$ -methyl-*n*-caproic acid (1:1136) q.v. (for the amide, anilide, and other derivatives corresponding to  $\bar{\text{C}}$  see 1:1136).

3:8355 (1) Dewael, Weckering, *Bull. soc. chim. Belg.* 33, 501-502 (1924). (2) Levene, Rothen, Marker, *J. Biol. Chem.* 115, 261-262 (1936).



B.P. 168-169° at 760 mm. (calcd.) (1)

 $D_4^{24.5} = 1.1003$  (1)

170-172° (2)

 $n_D^{21} = 1.4562$  (1)

101-102° at 100 mm. (1)

67-69° at 18-20 mm. (3)

3: 8340 3-CHLORO-2-METHYLPROPEN-2-OL-1  $\text{CH}_3$   $\text{C}_4\text{H}_7\text{OCl}$  Beil. I-443  
( $\gamma$ -Chloro- $\beta$ -methyl-allyl alcohol)



$I_1 -$   
 $I_2 -$

High-boilg. (*cis* ?)

B.P.

167-167.5° (1)

$D_4^{25} = 1.1262$  (2)  $n_D^{20} = 1.4730$  (2)

166-168° cor. (2)

163-164° (3)

$D_4^{20} = 1.1243$  (1)  $n_D^{20} = 1.4677$  (1)

Low-boilg. (*trans* ?)

B.P.

160-162° cor. (2)

$D_4^{25} = 1.1290$  (2)  $n_D^{20} = 1.4737$  (2)

[For prepn. of  $\bar{C}$  (mixt. of both forms) from 1,2,3-trichloro-2-methylpropane (3:5885) in 84% yield by hydrolysis with excess 5% aq. NaOH see (2) (4); for prepn. of  $\bar{C}$  from 1,3-dichloro-2-methylpropene-1 (3:5590) by hydrolysis with aq. alk. (4), with aq.  $\text{Na}_2\text{CO}_3$  (3), or aq. +  $\text{CaCO}_3$  (1) see indic. refs. Note that by virtue of allylic transposition 1,3-dichloro-2-methylpropene-1 (3:5590) may frequently yield derivatives of its syntenic isomer, 1,1-dichloro-2-methylpropene-2 (3:7480).]

$\bar{C}$  with excess AcOH + conc. HCl gives (60% yield (2)) 1-chloro-2-methylpropen-2-yl-1 acetate, b.p. 167-174° at 748 mm. (2), 176-178° at 784 mm. (1).

$\bar{C}$  on treatment with acids as specified (5) gives 3-chloro-2-methylpropanal-1 ( $\beta$ -chloro-isohutyraldehyde) (3:9112).

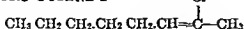
① 1-Chloro-2-methylpropen-2-yl-1 3,5-dinitrobenzoate: from high-boilg. form of  $\bar{C}$ ; m.p. 63.8-64.5° (2); from low-boilg. form of  $\bar{C}$ ; m.p. 94.4-95.8° (2).

② 1-Chloro-2-methylpropen-2-yl-1 *N*-phenylcarbamate: from high-boilg. form of  $\bar{C}$ ; m.p. 81-82° (1).

3:8340 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, II 4223; *C.A.* 33, 4190 (1939). (2) Rogers, Nelson, *J. Am. Chem. Soc.* 58, 1030 (1936). (3) Pogorshelaki,

1531.

3:8345 2-CHLORO-OCTENE-2  $\text{Cl}$   $\text{C}_8\text{H}_{15}\text{Cl}$  Beil. I - 221



$I_1 -$   
 $I_2 - (200)$

B.P. 167-168° (1)

$D_{16}^{16} = 0.8923$  (2)  $n_D^{16} = 1.4424$  (2)

Some doubt exists as to whether this material is in fact  $\bar{C}$ , 2-chloro-octene-1, or a mixture of both.

[For prepn. of  $\bar{C}$  from octanone-2 (*n*-hexyl-methyl ketone) (1:5490) with  $\text{PCl}_5$  followed by distillation (1) or treatment with alkali (2) see indic. refs.]

$\bar{C}$  with alc. KOH yields (1) octyne-1 (*n*-hexylacetylene) (1:8105) or octyne-2 (*n*-amyl-methylacetylene) (1:8120).

[ $\bar{C}$  on protracted (16 days') standing with benzoyl hydrogen peroxide in ether yields (2) 2-chloro-2,3-epoxyoctane, b.p. 81-82° at 21 mm.,  $D_4^{16} = 0.9609$ ,  $n_D^{16} = 1.4359$  (2).]

3:8345 (1) Bchal, *Ann. chim.* (6) 15, 277-278 (1888). (2) Prileshaiev, *Ber.* 59, 197-198 (1926).

3:8373 ETHYL *d,l*- $\beta$ -CHLORO-*n*-BUTYRATE  $C_6H_{11}O_2Cl$  Beil. II - 277  
 $CH_3\overset{\underset{\text{Cl}}{|}}{CH}.CH_2.COOCH_2CH_3$  II<sub>1</sub>-(124)  
 II<sub>2</sub>-(253)

B.P. 169.5° (1)  $D_4^{20} = 1.0542$  (6)  $n_D^{20} = 1.4253$  (2)  
 168-169° (2) 1.0517 (3) 1.4247 (6)  
 168-169° at 745.4 mm. (3) 1.42458 (3)  
 168-169° at 741 mm. (4)  
 65-65.5° at 15 mm. (5)

[For prepn. of  $\bar{C}$  from ethyl *n*-butyrate (1:3127) with  $SO_2Cl_2$  + dibenzoyl peroxide in  $CCl_4$  (50%  $\bar{C}$  together with 10%  $\alpha$ - and 40%  $\gamma$ -isomers) see (2); from  $\beta$ -chloro-*n*-butyric acid (3:0035) with EtOH + HCl see (4); from  $\beta$ -chloro-*n*-butyronitrile with EtOH + HCl or ethyl crotonate (1:3196) with HCl see (7) (9); from crotonic acid (1:0425) + EtOH + HCl see (3); from crotonyl chloride (3:7693) with EtOH see (8); from ethyl acetoacetate (1:1710) with Zn/Hg + alc. HCl (together with other prods.) see (10).]

$\bar{C}$  on htg. at 70-80° in s.t. with 9 vols. conc. alc.  $NH_3$  yields (12) (13) (10)  $\beta$ -amino-*n*-butyramide [Beil. IV-412], sirup (chloroplatinate, pale yel. ndls. from alc., % Pt. 31.78 (10) (12)).

$\bar{C}$  on hydrolysis (e.g., with aq. KOH (11)) yields EtOH (1:6130) and crotonic acid (1:0425), m.p. 72°, together with a little  $\beta$ -hydroxy-*n*-butyric acid.

3:8373 (1) Weidel, Roithner, *Monatsh.* 17, 188 (1896). (2) Price, Schwarcz, *J. Am. Chem. Soc.* 62, 2894-2895 (1940). (3) Brühl, *Ann.* 203, 27-28 (1880). (4) Balbiano, *Ber.* 10, 1749 (1887). (5) Lovén, *Ber.* 32 (1935). (7) Henry, *Bull. acad. roy. E* 84. (10) Steinkopf, *Ber.* 11, 348 (1878). (12) Balbiano, *Ber.* 13, 312 (1880); *Gazz. chim. ital.* 10, 137 (1880). (13) Scheibler, Magasanlk, *Ber.* 48, 1812 (1915).

3:8375 ISOBUTYL CHLOROACETATE  $C_6H_{11}O_2Cl$  Beil. II - 198  
 $(CH_3)_2CH.CH_2O.CO.CH_2Cl$  II<sub>1</sub>-( 89)  
 II<sub>2</sub>-

B.P. 170° at 760 mm. (1)  $D_4^{20} = 1.0612$  (2)  $n_D^{20} = 1.4255$  (2)  
 $D_4^{15} = 1.0675$  (1)

Colorless liq. with agreeable odor; insol. aq.; sol. alc., ether.

[For prepn. from isobutyl alc. (1:6165) + chloroacetic ac. (3:1370) + conc.  $H_2SO_4$  see (1).]

For study of hydrol. by dil. aq. halogen acids see (3).

3:8375 (1) Steinlen, *Bull. acad. roy. Belg.* (3) 34, 103 (1897); *Cent.* 1897, II 659. (2) Schjanberg, *Z. physik. Chem. A*-172, 228 (1935). (3) Drushel, Hill, *Am. J. Sci.* (4) 30, 72-78 (1910); *C.A.* 4, 2438 (1910).

[For formn. of  $\tilde{C}$  from 2-methylbutane (isopentane) (1:8500) with  $Cl_2$  (together with 2,3-dichloro-2-methylbutane (3:7975) and 2,4-dichloro-2-methylbutane (3:8105)) see (3); for formn. of  $\tilde{C}$  (together with other products) from dextrorotatory 1-chloro-2-methylbutane (*act.*-amyl chloride) by chlorination with  $SO_2Cl_2$  + benzoyl peroxide see (1); for formn. of  $\tilde{C}$  (together with other products) from 4-chloro-2-methylbutane (isoamyl chloride) (3:7365) +  $Cl_2$  in light see (2).] [The dextrorotatory form of  $\tilde{C}$  has been obtd. (4) from  $N,N'$ -dibenzoyl-2-methyltetramethylenediamine with  $PCl_5$ ]

$\tilde{C}$  on boilg. with  $AgOAc$  gives (3) a diacetate which upon saponification and subsequent oxidn. gives (3) methylsuccinic acid [Beil. II-637; II-(274)], m.p. 112°.

3:8360 (1) Brown, Kharsach, Chao, *J. Am. Chem. Soc.* 62, 3437-3439 (1940). (2) Perkin, *J. Soc. Chem. Ind.* 31, 616-624 (1912), *Cent.* 1912, II (1912). (3) Davydova, Papkins, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 7, 1992-1994 (1937); *Cent.* 1939, I 2397; *C.A.* 32, 482 (1938). (4) von Braun, Jostes, *Ber.* 59, 1095-1096 (1926).

3: 8365 **2-METHYL-*n*-CAPROYL CHLORIDE**  $C_7H_{13}OCl$  Beil. II - 342  
(Isoheptanoyl chloride; isoamylacetyl chloride)  $CH_3 \cdot \underset{\text{CH}_3}{CH} \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot \underset{\text{Cl}}{C=O}$  II-  
II-

B.P. 168-169° at 739 mm. (1)

[For prepn. of  $\tilde{C}$  from isoamylacetic acid [Beil. II-342, II-(146)] with  $PCl_5$  (1) or with  $SOCl_2$  (2) see indic. refs.]

$\tilde{C}$  with MeOH yields methyl isoheptanoate, b.p. 166-167.5° cor. (3);  $\tilde{C}$  with EtOH yields ethyl isoheptanoate, b.p. 181.5-182.5° cor. (3), 182.7° cor. at 750 mm (4); for reactn. of  $\tilde{C}$  with benzyl alc., phenylethyl alc., phenylpropyl alc., geraniol, and terpineol to give corresp. esters see (5)]

$\tilde{C}$  on hydrolysis yields isoamylacetic acid (see above), b.p. 216° cor. at 762 mm. (4).

Ⓐ Isoamylacet-amide: cryst. from aq.,  $AcOEt$ , or  $CCl_4$ , m.p. 103° (7), 103.5-104° cor. (4), 102-103° (6).

Ⓒ Isoamylacet-anilide: cryst. from ether + pet. ether, m.p. 74-75° (7), 75° (6).

Ⓓ Isoamyl acet-*p*-toluidide: ndls. from dil. alc, m.p. 75° (8).

3:8365 (1) Ponzio, de Gaspari, *Gazz. chim. ital.* 28, II 277 (1898). (2) Staudinger, Muntwyler, Kupfer, *Helv. Chim. Acta* 5, 761 (1922). (3) Poetsch, *Ann.* 218, 65-70 (1883). (4) Levene, Allen, *J. Biol. Chem.* 27, 442 (1916). (5) Rothstein, *Bull. soc. chim.* (4) 53, 1106-1107 (1938). (6) Wallach, *Ann.* 408, 190 (1915). (7) Fournier, *Bull. soc. chim.* (4) 5, 925 (1909). (8) Fichter, Rosenberger, *J. prakt. Chem.* (2) 74, 324 (1906).

3: 8370 ***d,l*-3-(CHLOROMETHYL)HEPTANE**  $C_8H_{17}Cl$  Beil. S.N. 10  
(2-Ethylhexyl chloride;  
1-chloro-2-ethylhexane)  $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot \underset{\text{H}}{\overset{CH_2Cl}{C}} \cdot CH_2 \cdot CH_3$

B.P. 169° (1)

73° at 18 mm. (1)

[For prepn. of  $\tilde{C}$  from 2-ethylhexanol-1 (1:6248) with  $SOCl_2$  + dimethylaniline see (1).]

3:8370 (1) Weizmann, Bergmann, Haskelberg, *Chemistry & Industry* 56, 589 (1937).

## CHAPTER XIX.

### DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

#### Section 2. $D_4^{20}$ less than 1.1500

(3:8500-3:8999)

3:8500	<i>d,l</i> -1-CHLOROPENTANOL-3 ( $\beta$ -Chloroethyl-ethyl-carbinol)	$\begin{array}{c} \text{C}_6\text{H}_{11}\text{OCl} \\ \text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{Cl} \end{array}$	Beil. I — I <sub>1</sub> -(194) I <sub>2</sub> -(421)
B.P. 173°	at 760 mm. (1)	$D_4^{25} = 1.0327$ (2)	$n_D^{25} = 1.466$ (3)
100°	at 60 mm. (1)	1.035 (3)	1.448 (2)
77.0-77.5°	at 20 mm. (2)		
70-71°	at 10 mm. (3)		

Liquid with weak odor resembling that of allyl alcohol. — Sparingly sol. cold aq.; sol. hot aq.

[For prepn. of  $\bar{C}$  from  $\beta$ -chloropropionat . . . . .]

[ $\bar{C}$  with AcCl yields (1) 3-acetoxy-1-chl

4 hrs. at 160-170° with KOAc yields (4) 1-

$\bar{C}$  with BzCl yields (1) 3-benzyloxy-1-chloropentane, b.p. 168° at 15 mm. (1), while C htd. to 180° for 10 hrs. with NaOBz + KI yields (4) 1-benzoxypentanol-3, b.p. 181° at 20 mm., 171° at 11 mm. (4).]

[For reactn. of  $\bar{C}$  with alk.  $\text{Na}_3\text{AsO}_3$  see (3).]

[ $\bar{C}$  with  $\text{COCl}_2$  yields (5) the corresp. chloroformate, b.p. 95° at 18 mm., which with excess  $\text{NH}_3$  gives  $\beta$ -chloroethyl-ethyl-carbinyl carbamate, m.p. 68° (5).]

3:8500 (1) Fourneau, Ramart-Lucas, *Bull. soc. chim.* (4) 25, 366-368 (1919). (2) Lespieau, *Bull. soc. chim.* (5) 7, 254-258 (1940); *C.A.* 34, 5414 (1940). (3) Baeker, Bolt, *Rec. trav. chim.* 54, 70 (1935). (4) Fourneau, Ramart-Lucas, *Bull. soc. chim.* (4) 27, 554-556 (1920). (5) Puyal, Montagne, *Bull. soc. chim.* (4) 27, 859 (1920).

3:8510	1-CHLORO-4-ETHYLHEXENE-3	$\text{C}_8\text{H}_{15}\text{Cl}$	Beil. I — I <sub>1</sub> — I <sub>2</sub> -(201)
	$\begin{array}{c} \text{Cl} \qquad \qquad \text{CH}_2\text{CH}_3 \\   \qquad \qquad   \\ \text{CH}_2\text{CH}_2\text{CH}=\text{C}-\text{CH}_2\text{CH}_3 \end{array}$		

B.P. 173° (1)

$D_4^{20} = 0.9102$  (1)  $n_D^{20} = 1.4524$  (1)

[For prepn. of  $\bar{C}$  from 6-chlorohexanone-3 ( $\gamma$ -chloro-*n*-propyl ethyl ketone) [Beil. I- (355), I<sub>2</sub>-(747)] with excess  $\text{EtMgBr}$  see (1).]

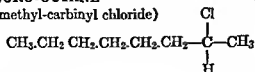
$\bar{C}$  adds  $\text{Br}_2$ .

3:8510 (1) De Boosere, *Bull. soc. chim. Belg.* 32, 35-39 (1923).

3:8378 *d,l*-2-CHLORO-OCTANE  
(*n*-Hexyl-methyl-carbinyl chloride)

 $C_8H_{17}Cl$ 

Beil. I - 160

I<sub>1</sub>—I<sub>2</sub>-(124)

B.P. 171-173° cor. (1)

 $D_{25}^{25} = 0.86388$  (1)

169-171° (2)

55-56° at 14 mm. (3)

 $D_{15}^{15} = 0.87075$  (1)

[For prepn of  $\bar{C}$  from octanol-2 (*n*-hexyl-methyl-carbinol) (1:6245) with HCl (4) (5), with  $PCl_5$  (4) (6), or with  $SOCl_2$  in pyridine (3) see indic. refs.; for prepn. of  $\bar{C}$  from octene-1 + HCl +  $AlCl_3$  see (7).] [The large amt. of work on the opt. act. isomers of  $\bar{C}$  cannot be discussed here; see Beil. I<sub>1</sub>-(60), I<sub>2</sub>-(124) and subsequent literature incl. (8).]

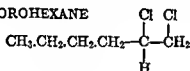
[For study of rate of reactn. of  $\bar{C}$  with KI in acetone see (2).]

3:8378 (1) Perkin, *J. prakt. Chem.* (2) 31, 495 (1885). (2) Conant, Hussey, *J. Am. Chem. Soc.* 47, 485 (1925). (3) McKenzie, Tudhope, *J. Biol. Chem.* 62, 554 (1924/25). (4) Bouis, *Ann.* 92, 398 (1854). (5) Malbot, *Bull. soc. chim.* (3) 3, 69 (1890). (6) Dachauer, *Ann.* 106, 270 (1858). (7) Webb (to Carbide and Carbon Chem. Corp), U.S. 1,560,625, Nov. 10, 1925, *Cent.* 1926, I 1713, *C.A.* 20, 51 (1926). (8) Gerrard, *J. Chem. Soc.* 1944, 85-90, 1945, 106-112.

3:8380 *d,l*-1,2-DICHLOROHEXANE

 $C_6H_{12}Cl_2$ 

Beil. I - 144

I<sub>1</sub>—I<sub>2</sub>—

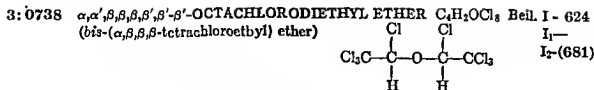
B.P. 172-174° (1)

 $D_{15}^{15} = 1.085$  (1)

[For prepn. of  $\bar{C}$  from hexene-1 (1:8255) +  $Cl_2$  see (1).]

3:8380 (1) Brochet, *Bull. soc. chim.* (3) 7, 569 (1892).





M.P. 47° (1) B.P. 130-131° at 11 mm. (1)  
45-46° (1) 128-130° at 9 mm. (1)  
40-42° (2)

Cryst. with agreeable camphoraceous odor from MeOH or EtOH. — Eas. sol. MeOH,  $C_6H_6$ , toluene, or pct. ether; spar. sol. in abs. alc. below 0°.

$\bar{C}$  slowly sublimes but on attempted distn. at ord. press. decomposes at about 240°.

[For prepn. of  $\bar{C}$  from chloral (3:5210), chloral hydrate (3:1270), or metachloral with  $ClSO_3H$  or  $FSO_3H$  at not above 50-60° see (1); note that from chloral (3:5210) with  $ClSO_3H$  at -50° for 10-12 hrs. yield of  $\bar{C}$  may be as high as 50%; from metachloral with  $ClSO_3H$  at 50° for a few hrs. yield is 60% (1); note also that various other products including chloralide (3:3510) are also formed. — For farmn. of  $\bar{C}$  from trichloroethylene (3:5170) with excess  $Cl_2O$  in  $CCl_4$  at -20° (2), or perhaps from  $\alpha,\alpha'$ -dichlorodiethyl ether (3:7595) with  $Cl_2$  in sunlight (3), see indic. refs.]

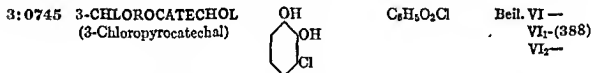
$\bar{C}$  on htg. in pres. of air gives (2) phosgene (3:5000).

$\bar{C}$  on reduction with conc. HI ( $D = 1.78$ ) in hailg. AcOH quantitatively yields (2) ethane.

$\bar{C}$  is fairly stable toward hailg. aq. or aq. alkalies (1).

$\bar{C}$  is claimed (1) to react with 2 moles of  $RMgX$  cpds. of either aliphatic or aromatic types, but no details are reported.

3:0738 (1) Fuchs, Katscher, *Ber.* 62, 2381-2386 (1929). (2) Goldschmidt, Schussler, *Ber.* 58, 569-570 (1925). (3) Roth, *Ber.* 8, 1017-1018 (1875).



M.P. 47° (1) B.P. 110-111° at 11 mm. (2).  
46-48° (2)

White cryst. (from pct. ether) (1); hygroscopic scales (from lgr.) (2). — Eas. deliquesces absorbing  $\frac{1}{2}$  mole  $H_2O$ . — Eas. sol. aq. but insol. almost all org. solvents except cold pct. ether or cold lgr.

[For prepn. from catechol (1,2-dihydroxybenzene) (1:1520) by action of  $SO_2Cl_2$  in ether at 0° see (1) (2); for prepn. from *o*-benzoquinone [Beil. VII-600] by action of ethereal HCl see (2); 4-chlorocatechol (3:2470) is also a by-product of both methods.]

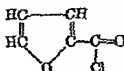
[ $\bar{C}$  on oxido. with  $PhO_2$  in pct. ether gives (12% yield (2)) 3-chloro-*o*-benzoquinone [Beil. VII<sub>1</sub>-(388)]; for use in prepn. of  $\alpha$ -chlorophenazine see (1).]

$\bar{C}$  with  $FeCl_3$  gives a blue-green color, changing to clear red on addn. of  $Na_2CO_3$  (2).

③ 3-Chloropyrocatechol dibenzoate: ndls. from alc., m.p. 108-109° (2); 109° u.c. (1).

3:0745 (1) Wrede, Mühlroth, *Ber.* 63, 1932-1933 (1930). (2) Willstätter, Müller, *Ber.* 44, 2184-2189 (1911).

3:8515 FUROYL CHLORIDE  
(Pyromucyl chloride;  
furan 2-carboxylic  
acid chloride)


 $C_5H_3O_2Cl$ 

Beil. XVIII-276  
XVIII<sub>1</sub>—

B.P. 173-174° (1)  
173° (2) (3)  
170° (4)  
58° at 12 mm. (5)  
66° at 10 mm. (6)  
59.5-61.5° at 7 mm. (7)

M.P. -2° (8)

Colorless strongly refractive liquid rapidly decomposed in strong light (7).— $\bar{C}$  is stronger lachrymator than  $BzCl$  (2).

[For prepn. of  $\bar{C}$  from furoic acid (1:0475) with  $PCl_5$  (poor yields (3) (4) (6)), with excess  $PCl_5$  in dry  $CHCl_3$  as specified (100% yield (6)) (8), with  $PCl_5$  (77% yield (5)), with  $SOCl_2$  (100% (2), 79% (1), 60% (3)), with  $SOCl_2$  in  $C_6H_6$  (89.5% yield (7)), or with phosgene (9) see indic. refs.]

[ $\bar{C}$  with  $MeOH$  yields methyl furoate (1:3452), b.p. 180.5° at 750 mm., 76° at 20 mm.,  $D_4^{20} = 1.1792$ ,  $n_D^{20} = 1.4575$  (10);  $\bar{C}$  with  $EtOH$  yields ethyl furoate (1:2082), b.p. 197°, m.p. 34°;  $\bar{C}$  with furfuryl alc. (1:6425) yields (11) furfuryl furoate, dimorphous cryst., m.p. 27.5° and 19.5°, b.p. 122° at 2 mm. (11); for study of reactn. of  $\bar{C}$  with cellulose see (12)]

[ $\bar{C}$  with phenol yields (2) phenyl furoate, m.p. 41.5° (2)]

[ $\bar{C}$  with  $C_6H_6 + AlCl_3$  yields (13) (14)  $\alpha$ -furyl phenyl ketone [Beil. XVII-348; XVII<sub>1</sub>-(186)], b.p. 282-284°;  $\bar{C}$  with toluene +  $AlCl_3$  gives (80% yield (15))  $\alpha$ -furyl p-tolyl ketone, m.p. 41-42°, b.p. 180-183° at 23 mm. (15)]

[For study of reactn. of  $\bar{C}$  with  $Cl_2$  (16) or  $Br_2$  (17) see indic. refs.]

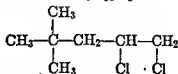
$\bar{C}$  with pyridine in ether or  $\bar{C}$  with  $Na$  or  $Ag$  furoate yields (18) furoic anhydride, ndls. from alc., m.p. 73° (18).

$\bar{C}$  on hydrolysis (rate of reactn. even with boilg. aq. slower than  $BzCl$  (6)) yields furoic acid (1:0475), m.p. 133-134° (for the amide, anilide, p-toluidide, and other derivatives corresp. to  $\bar{C}$  see 1:0475).

3:8515 (1) Bogert, *Stull. J. Am. Chem. Soc.* 49, 252 (1925). (2) Baum, *Ber.* 37, 2951 (1904), (3) Gellisen, van Roon, *Rec. trav. chim.* 43, 361 (1924). (4) Liè-Bodart, *Ann.* 190, 327 (1856); *Compt. rend.* 43, 393 (1856). (5) Reichstein, Moorman, *Helv. Chim. Acta* 17, 1122 (1934). (6) Frankland, Aston, *J. Chem. Soc.* 79, 516-517 (1901). (7) Hartmann, Dickey, *Ind. Eng. Chem.* 24, 151-152 (1932). (8) Chavasse, *Compt. rend.* 134, 1439 (1902). (9) Meuser (to Dominion Rubber Co.), Canadian 373,516, May 3, 1938; *Cent. 1938*, II 3609; *C.A.* 32, 5003 (1938). (10) Price, Chapin, Goldman, Krebs, Shafer, *J. Am. Chem. Soc.* 63, 1659 (1941).

(11) Zanetti, *J. Am. Chem. Soc.* 47, 1452-1453 (1925). (12) Kobe, Montonna, *J. Am. Chem. Soc.* 53, 1859-1891 (1931). (13) Marquis, *Bull. soc. chim.* (3) 23, 33 (1906); *Ann. chim.* (8) 4, 276-277 (1905). (14) Gilman, Hewlett, *Iowa State Coll. J. Sci.* 4, 27-33 (1929); *Cent. 1931*, II 1428; *C.A.* 24, 1640 (1930). (15) Borsche, Leditsche, *Ann.* 579, 110 (1937). (16) Hewlett, *Iowa State Coll. J. Sci.* 6, 439-445 (1932). *Cent. 1933*, I 942. *C.A.* 27, 979-980 (1933). (17) Shepard, Winslow, Johnson, *J. Am. Chem. Soc.* 52, 2083-2090 (1930). (18) Baum, *Ber.* 34, 2505 (1901).

3:8516 *d,l*-4,6-DICHLORO-2,2-DIMETHYLPENTANE  $C_7H_{14}Cl_2$  Beil. S.N. 10  
(1,2-Dichloro-4,4-dimethylpentane)



B.P. 173-175° at 746 mm. (1)  
58-59° at 12 mm. (1)

$D_4^{20} = 1.0259$  (1)  $n_D^{20} = 1.4489$  (1)

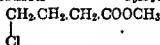
[For prepn. of  $\bar{C}$  from allyl chloride (3:7035) with 2-methylpropane (isobutane) +  $AlCl_3$  at  $-10^\circ$  (13-15% yield accompanied by 35-40% yield of 5-chloro-2,3-dimethylpentane (3:8153)), or with *tert*-butyl chloride (3:7045) +  $AlCl_3$  at  $-10^\circ$  to  $-20^\circ$ , see (1).]

[ $\bar{C}$  with isobutane +  $AlCl_3$  gives (1) a mixt. of products including *tert*-butyl chloride (3:7045), 5-chloro-2,3-dimethylpentane (3:8153), etc.]

$\bar{C}$  with Zn dust + alc. reacts only very slowly under reflux but in s.t. at  $120^\circ$  gives (45% yield (1)) 4,4-dimethylpentene-1 (1:8285), b.p.  $71.8^\circ$  (1).

3:8516 (1) Schmerling, *J. Am. Chem. Soc.* 67, 1438-1441 (1945).

3:8517 METHYL  $\gamma$ -CHLORO-*n*-BUTYRATE  $C_5H_9O_2Cl$  Beil. II-278



II<sub>1</sub>-  
II<sub>2</sub>-

B.P. 175-176° at 764 mm. (1)  
173-174° (2)  
172-174° at 749 mm. (3)  
102-105° at 58 mm. (3)  
90° at 46 mm. (4)  
55-56° at 7 mm. (5)

$D_4^{14} = 1.1268$  (1)  $n_D^{20} = 1.4324$  (4)

$D_4^{20} = 1.1804$  (2)

[For prepn. of  $\bar{C}$  from  $\gamma$ -chloro-*n*-butyronitrile with MeOH + HCl (80% yield (4)) (2) see indic. refs.; from  $\gamma$ -methoxy-*n*-butyric acid (3) by btg. with  $SOCl_2$  for 6 hrs. (86% yield (3)) or by htg.  $\gamma$ -methoxy-*n*-butyryl chloride (84% yield (3)) see (3); from  $\gamma$ -hydroxy-*n*-butyronitrile with MeOH + HCl see (5).]

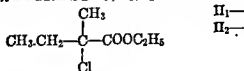
$\bar{C}$  on 48-hr. reflux with alc. KOH gives (67.5% yield (3))  $\gamma$ -butyrolactone (1:5070), b.p.  $206^\circ$ .

[ $\bar{C}$  refluxed 8 hrs. with NaI in acetone gives (3) methyl  $\gamma$ -iodo-*n*-butyrate, b.p.  $80-83^\circ$  at 11 mm. (3);  $\bar{C}$  with 4 moles MeMgCl in ether yields (4) 5-chloro-2-methylpentanol-2.]

$\bar{C}$  on hydrolysis by boilg. 6 hrs. with conc. HCl gives (32% yield (3))  $\gamma$ -chloro-*n*-butyric acid (3:0020) q.v.

For the amide, anilide, *p*-toluidide, and other derivatives corresp. to  $\bar{C}$  see  $\gamma$ -chloro-*n*-butyric acid (3:0020).

3:8518 ETHYL  $d,l$ - $\alpha$ -CHLORO- $\alpha$ -METHYL- $n$ -BUTYRATE  $C_7H_{13}O_2Cl$  Beil. II-306



B.P. 175° at 747 mm. (1)

$D_4^{14} = 1.069$  (1)

$n_D^{11} = 1.43683$  (1)

Oily liq.; insol. aq.; sol. alc., ether.

[For prepn. of  $\bar{C}$  from  $\alpha$ -chloro- $\alpha$ -methyl- $n$ -butyronitrile with EtOH + HCl see (1).]

For the corresp. acid,  $\alpha$ -chloro- $\alpha$ -methyl- $n$ -butyric acid see 3:8718.

3:8518 (1) Servais, *Rec. trav. chim.* 20, 60 (1901).

3:8520  $n$ -HEPTANOYL CHLORIDE  $\text{CH}_3(\text{CH}_2)_5\text{C}=\text{O}$   $C_7H_{13}\text{OCl}$  Beil. II-340  
(Enanthoyl chloride)



$\Pi_1- \\ \Pi_2-$

B.P.	F.P.		
175.2° at 760 mm. (1)	-83.8° (1)	$D_4^{25} = 0.95694$ (1)	
175.0° (2)			
174-175° (3)		$D_4^{20} = 0.96170$ (1)	
77° at 23 mm. (4)			
74-75° at 19 mm. (5)		$D_4^{15} = 0.96645$ (1)	$n_D^{15} = 1.43447$ (2)
59-61° at 11 mm. (6)		0.9669 (2)	
56° at 8 mm. (7)			

[For prepn. of  $\bar{C}$  from heptanoic acid (enanthic acid) (1:1140) with  $\text{PCl}_5$  (2) (51% yield (8)), with  $\text{PCl}_3$  (75% yield (1)), with  $\text{PCl}_3 + \text{ZnCl}_2$  (89% yield (8)), or with  $\text{SOCl}_2$  (yield 98.5% (6), 80% (8)) see indic. refs.]

[For reactn. of  $\bar{C}$  with various higher alcohols see (9), with various acylureas see (10), with vanillylamine see (11) (5), with sodium  $n$ -heptylate to yield  $n$ -heptylic anhydride (1:1165), b.p. 258°, see (1) (2).]

[ $\bar{C}$  with  $\text{AlCl}_3 + \text{phenol}$  yields (12) 48%  $o$ -( $n$ -heptanoyl)phenol, b.p. 172-174° at 20 mm. (13), 155-156° at 10 mm. (12), m.p. 24° (13), +9.8° (12),  $D_4^{24} = 1.0110$  (12),  $n_D^{25.5} = 1.5209$  (12) (phenylhydrazone, m.p. 91-92° (13), semicarbazone, m.p. 162° (12)), and 41%  $p$ -( $n$ -heptanoyl)phenol, m.p. 93-94° (13), 91-91.5° (12), b.p. 220° at 15 mm. (13) (acetate, m.p. 46.5° (12), benzoate, m.p. 96.5-97° (12), 92-93° (13)).]

[ $\bar{C}$  on warming with  $\text{NaN}_3$  in  $\text{C}_6\text{H}_6$  yields (14)  $n$ -hexyl isocyanate, b.p. 163-164° (14), and/or (15)  $n$ -hexylamine  $\text{HCl} + N,N'$ -di- $n$ -hexylurea, m.p. 58-59° (15).]

[ $\bar{C}$  in ether treated with diazomethane as directed (7) yields 1-chlorooctanone-2, b.p. 91-96° at 10 mm. (7).]

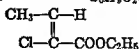
$\bar{C}$  on hydrolysis yields  $n$ -heptanoic (enanthic) acid (1:1140) q.v. (for the amine, amide,  $p$ -toluidide, and other derivatives corresp. to  $\bar{C}$  see 1:1140).

3:8520 (1) Deffet, *Bull. soc. chim. Belg.* 40, 389-394 (1931). (2) Lumsden, *J. Chem. Soc.* 87, 92-93 (1905). (3) Freundler, *Bull. soc. chim.* (3) 13, 833 (1895). (4) Krafft, *Ber.* 19, 2987 (1886). (5) Ford-Moore, Phillips, *Rec. trav. chim.* 53, 855 (1934). (6) Fierz-David, Kuster, *Helv. Chim. Acta* 22, 86-89 (1939). (7) Spath, Lorenz, *Ber.* 74, 599-603 (1941). (8) Clark, Bell, *Trans. Roy. Soc. Can.* (3) 27, III 97-103 (1933). (9) Rothstein, *Bull. soc. chim.* (4) 53, 1106-1107 (1933). (10) Stoughton, *J. Org. Chem.* 2, 514-521 (1938).

(11) Nelson, *J. Am. Chem. Soc.* 41, 2124 (1919). (12) Sandulesco, Girard, *Bull. soc. chim.* (4) 47, 1305-1310 (1930). (13) Coulthard, Marshall, Pyman, *J. Chem. Soc.* 1930, 280-291. (14) Schroeter, *Ber.* 42, 3358 (1909). (15) Nelles, *Ber.* 65, 1346-1347 (1932).

3:8523 ETHYL  $\alpha$ -CHLOROCROTONATE $C_6H_9O_2Cl$ 

Beil. II - 415

 $\Pi_1$ -(189) $\Pi_2$ -(395)

B.P.

B.P. (contd.)

176-178°	(1)	85° at 36 mm.	(3)	$D_4^{20.1} = 1.1086$	(8)	
175-177°	(2)	67-68° at 15 mm.	(2)			$n_D^{20.1} = 1.45303$ (8)
176° at 760 mm.	(3)	72° at 14 mm.	(8)	$D_4^{20} = 1.100$	(8)	
176°	(4)	61° at 10 mm.	(9)	1.102	(9)	
175-176° cor.	(5)			$D_4^{19.8} = 1.1133$	(6)	
175.0-175.5°	(6)					$n_D^{19.8} = 1.45378$ (6)
				$D_4^{14.3} = 1.1073$	(9)	

[See also ethyl  $\alpha$ -chloroisocrotonate (3:9368).]

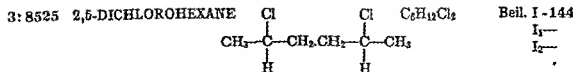
[For prepn. of  $\bar{C}$  from  $\alpha$ -chlorocrotonic acid (3:2760) in EtOH with dry HCl gas (4) (5) (8) or with conc.  $H_2SO_4$  (9) see indic. refs.; from  $\alpha$ -chloroisocrotonic acid (3:1615) in EtOH with conc.  $H_2SO_4$  at 100° (note isomerization) see (9); from the ethyl ester of the lower-melting (63°)  $\alpha,\beta$ -dichloro-*n*-butyric acid (3:1375) in EtOH with KCN (1 mole) for 10 min. (75% yield) see (3); from ethyl  $\alpha,\alpha,\beta$ -trichloro-*n*-butyrate (3:6380) with Zn in moist ether (100% yield) see (10); from  $\alpha,\alpha,\beta$ -trichloro-*n*-butyraldehyde (butylchloral) (3:5910) (1) as hydrate (3) or cyanohydrin (3) in EtOH with KCN (2 moles) below 15° (85% yield (3)) see indic. refs.; from ethyl  $\alpha$ -chloro- $\alpha$ -vinylacetate (2) by isomerization of the double bond with NaOAc/AcOH under reflux 30-40 hrs. see (2).]

[ $\bar{C}$  with Al/Hg in alc. gives (11) crotonic acid (1:0425), m.p. 72°.]

$\bar{C}$  with diazomethane in dry ether does not react (12); however, upon addn. of a drop of water addition of  $CH_2N_2$  to unsatd. linkage takes place with elimination of HCl (on distillation) yielding (12) ethyl 4-methylpyrazole-3-(5)-carboxylate [Beil. XXV-117, m.p. 156-157° (12).]

[ $\bar{C}$  with piperidine (3 moles) in abs. alc. stood 3 hrs. then neutralized, etc., (13) gives (by reactn. of 1 piperidine with the halogen and addition of a second molecule of piperidine to the unsatd. linkage (or vice versa)) (63% yield (13)) ethyl  $\alpha,\beta$ -di-piperidino-*n*-butyrate, viscous oil, insol. aq., b.p. 181-183° at 14 mm.]

3:8523 (1) Wallach, *Ann.* **173**, 301 (1874). (2) Rambaud, *Bull. soc. chim.* (5) **1**, 1353-1354 (1934). (3) Chattaway, Irving, *J. Chem. Soc.* **1929**, 1043-1045. (4) Sarnow, *Ann.* **164**, 101 (1872). (5) Perkin, *J. Chem. Soc.* **65**, 424 (1894). (6) Eisenlohr, *Ber.* **44**, 3208 (1911). (7) Roberts, *J. Chem. Soc.* **1938**, 779. (8) von Auwers, *Ber.* **45**, 2806 (1912). (9) von Auwers, *Ann.* **432**, 61 (1923). (10) Michael, Schulthess, *J. prakt. Chem.* (2) **43**, 595 (1891). (11) Wislicenus, *J. prakt. Chem.* (2) **54**, 59-60 (1896). (12) von Auwers, König, *Ann.* **496**, 31, 41 (1932). (13) Roberts, *J. Chem. Soc.* **1938**, 963-964.

*d,l*-form

B.P.

176.4-177.4° cor. at 761.1 mm. (1)

$D_4^{25} = 1.0431$  (1)

62.0-62.5° at 12 mm. (2)

$D_4^{12} = 1.0529$  (2)  $n_D^{12} = 1.4495$  (2)

$D_4^0 = 1.0675$  (1)

*meso*-form

B.P.

M.P.

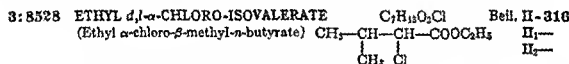
177.8-178.2° cor. at 761.8 mm. (1) 18.7° (1)

$D_4^{25} = 1.0459$  (1)

[For prepn. of  $\bar{C}$  (presumably mixt. of both diastereoisomers) from hexadiene-1,5 (biallyl) (1:8045) by shaking with 5 vols. conc. HCl for 120 hrs. at room temp. (57% yield accompanied by 23% 5-chlorohexene-1 (3:7665)) see (1), from 2,5-dimethyltetrahydrofuran [Beil. XVII-14] on protracted treatment with HCl gas +  $\text{ZnCl}_2$  (8% yield (3)) see (3).]

[For sepn. of *meso*- from *d,l*-form by cooling to  $-50^\circ$  see (1).][For behavior of  $\bar{C}$  on treatment with  $N/10$  aq. alc. KOH see (2).]

3:8525 (1) Cortese, *J. Am. Chem. Soc.* 52, 1519-1520 (1930). (2) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 9, 1380-1388 (1939); *C.A.* 34, 1611 (1940) (3) Fried, Kleene, *J. Am. Chem. Soc.* 63, 2691 (1941).



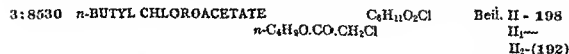
B.P. 177-179° at 766 mm. (1)

$D_4^{13.2} = 1.021$  (1)  $n_D^{11} = 1.42951$  (1)

Oil with odor like peppermint.

[For prepn. of  $\bar{C}$  from  $\alpha$ -chloro-isovaleric acid (3:0050) with EtOH +  $\text{H}_2\text{SO}_4$  see (1); for formn. from ethyl  $\alpha$ -diazo-isovalerate with HCl see (2).]

3:8528 (1) Servais, *Rec. trav. chim.* 20, 54 (1901). (2) Curtius, *J. prakt. Chem.* (2) 125, 254 (1930).



B.P. 178.2-179° at 727 mm. (1)

$D_4^{20} = 1.0704$  (4)  $n_D^{20} = 1.4301$  (4)

176.7° (2)

91° at 38 mm. (3)

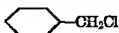
Colorless mobile liq. with fragrant odor. — Insol. aq., misc. with alc. or ether (5).

[For prepn. (97% yield (3)) from *n*-butyl alc. (1.6180) + chloroacetic ac. (3:1370) see (3).]

[For study of insecticidal action of vapor of  $\bar{C}$  see (6).]

3:8530 (1) Gustus, Stevens, *J. Am. Chem. Soc.* 55, 384-385 (1933). (2) Cheng, *Z. physik. Chem. B-24*, 307 (1934) (3) Liston, Dehn, *J. Am. Chem. Soc.* 60, 1264-1265 (1938). (4) Schjanberg, *Z. physik. Chem. A-172*, 228 (1935). (5) Gehring, *Bull. soc. chim.* (2) 46, 147 (1886). (6) Roark, Cotton, *Ind. Eng. Chem.* 20, 512-514 (1928).

3: 8535 BENZYL CHLORIDE  
( $\alpha$ -Chlorotoluene;  
 $\omega$ -chlorotoluene)

 $C_7H_7Cl$ 

Beil. V - 292  
V<sub>1</sub>-(151)  
V<sub>2</sub>-(227)

B.P.			F.P.		
179.35°	at 760 mm.	(1)	-37.5°	(23)	$D_4^{20} = 1.08977$ (24)
179.3°	at 760 mm.	(2)	-39.0°	(1)	1.08815 (28)
179° cor.		(3)	-39.2°	(24)	1.08699 (28)
179°	at 749 mm.	(4)	-39.7°	(7)	$D_4^{25} = 1.09460$ (24)
178.6-179.0°	at 766 mm.	(5)	-41.2°	(25)	1.100 (29)
178.5-179°		(5)	-43.2°	(25)	$n_D^{25} = 1.5363$ (21)
178.5°	at 764 mm.	(7)	-48.0°	(27)	$D_4^{20} = 1.09943$ (24)
178.0-178.5°		(8)			$n_D^{20} = 1.5391$ (31) (32)
177.5-178°	at 755 mm.	(142)			$n_D^{17.4} = 1.5391$ (33)
177.0-177.5° u.c.		(9)			$D_4^{15.4} = 1.1138$ (30)
175.2-178.3°		(28)			$n_D^{15.4} = 1.5415$ (30)
175-175.2°	at 769.3 mm.	(10)			$D_4^{15} = 1.10426$ (24)
174.0-174.8°		(28)			$n_D^{15} = 1.54124$ (24)
173° dec.		(11)			$D_L^I = 1.099$ (34)
172°	at 730 mm.	(12)			$n_D^I = 1.5415$ (34)
141°	at 261 mm.	(13)			
128°	at 163 mm.	(13)			See also Note 2.
118°	at 111 mm.	(13)			See also Note 3.
100.2°	at 92 mm.	(14)			
103°	at 76.1 mm.	(14)			Note 1. Despite an earlier report (1), $\bar{C}$ is later
96-99°	at 62 mm.	(15)			(34) stated to decompose so readily on heating
100°	at 59 mm.	(13)			that precise detn. of boiling point at 760 mm. is
93.3°	at 47.8 mm.	(14)			impracticable.
89.9°	at 40 mm.	(14)			
83.6°	at 28.64 mm.	(14)			Note 2. The presence of benzyl alc. (1:6480)
81.5-82°	at 28 mm.	(16)			lowers density; presence of HCl or of oxidation
81.8°	at 26.74 mm.	(14)			products raises density (24).
78.2°	at 22.1 mm.	(14)			
73.9°	at 17 mm.	(14)			Note 3. Values of $n_D^{20}$ for mixtures of $\bar{C}$ with
66-67°	at 16 mm.	(17)			benzal (di)chloride (3:6327) (for which $n_D^{20} =$
70.4-70.5°	at 15 mm.	(11)			1.5502) are linear with composition (31).
64.0-64.2°	at 12 mm.	(18)			
66°	at 11 mm.	(13)			
61-62°	at 11 mm.	(19)			
63.0°	at 8.2 mm.	(14)			
57-58°	at 8 mm.	(20)			
56-58°	at 4-5 mm.	(21)			
51-52°	at 4 mm.	(22)			

See also Note 1.

[See also benzal (di)chloride (3:6327) and benzotrichloride (3:6540).]

Colorless liq. with penetrating odor; vapor of  $\bar{C}$  is irritating to eyes. — Insol. aq., volatile with steam. — Insol. cold conc.  $H_2SO_4$ , but soon reacts evolving HCl.  $\bar{C}$  dissolves below -20° in equal vol. pet. ether (35).

Binary systems containing  $\bar{C}$ .  $\bar{C}$  + *toluene*: for b.p. and vapor press. relations see (36). —  $\bar{C}$  + *anisole*: for f.p./composition data see (25). —  $\bar{C}$  + *N-methylaniline*: for f.p./composition data see (25).

$\bar{C}$  with *benzaldehyde* (1:0195) forms a const.-boilg. mixt., b.p. 177.9° at 760 mm., contg. 50 wt. %  $\bar{C}$  (37-a). —  $\bar{C}$  with *n-butyric acid* (1:1035) forms a const.-boilg. mixt., h.p. 160.8° at 760 mm., contg. 35 wt. %  $\bar{C}$  (38). —  $\bar{C}$  with *isobutyric acid* (1:1030) forms a const.-boilg. mixt., h.p. 153.5° at 760 mm., contg. 20 wt. %  $\bar{C}$  (38). —  $\bar{C}$  with *n-caproic acid* (1:1130) forms a const.-boilg. mixt., b.p. 179.0° at 760 mm., contg. 97 wt. %  $\bar{C}$  (38).

$\bar{C}$  with *chloroacetic acid* (3:1370) forms a const.-boilg. mixt., b.p. 172° at 760 mm., contg. 72 wt. %  $\bar{C}$  (38-b). —  $\bar{C}$  with " $\alpha$ -dichlorohydrin" (1,3-dichloropropanol-2) (3:5985) forms a const.-boilg. mixt., h.p. 163.9° at 760 mm., contg. 43 wt. % (2)

### PREPARATION OF $\bar{C}$

From benzene. The prepn. of  $\bar{C}$  from benzene (1:7400) by direct introduction of the  $-\text{CH}_2\text{Cl}$  group (chloromethylation) has been much studied especially in recent years. Chloromethylation may be effected with paraformaldehyde (1:0080), formalin (1:0145), chloromethyl methyl ether (3:7085), or bis-(chloromethyl) ether (3:5245), each in the pres. of  $\text{ZnCl}_2$  and frequently also of  $\text{HCl}$  gas. For a general review of the process of chloromethylation see (39) and subsequent articles (32) (40) (41). Various by-products of the reaction are formed, notably  $\omega, \omega'$ -dichloro-*p*-xylene (3:2825) and diphenylmethane (1:7120). For study of further chloromethylation of  $\bar{C}$  to various poly-(chloromethyl)-benzenes see (41).

[For prepn. of  $\bar{C}$  from  $\text{C}_6\text{H}_6$  (1:7400) by chloromethylation with paraformaldehyde (1:0080) +  $\text{ZnCl}_2$  +  $\text{HCl}$  (yields: 80% (42), 73.5% (40), 70% (32), 36% (42)) (39), with formalin (1:0145) +  $\text{ZnCl}_2$  +  $\text{HCl}$  (yields: 70.5% (40), 57% (44)) (45) (39) (48), or with chloromethyl methyl ether (3:7085) (40) (43) (46) (47) or bis-(chloromethyl) ether (3:5245) (40) (43) see indic. refs.]

From toluene. [For prepn. of  $\bar{C}$  from toluene (1:7405) by chlorination with  $\text{SO}_2\text{Cl}_2$  in pres. of dibenzoyl peroxide (75–80% yield (15)), with  $\text{SO}_2\text{Cl}_2$  (for study of effect of catalysts see (83) (84)) below 130° (49) (50), with  $\text{SO}_2\text{Cl}_2$  in pres. of acetyl chloride (51), with  $\text{Cl}_2$  (52) (53) (for study of catalysts see (85)) in vapor phase (54) (55) (61) in light (56) (57) (58) (59) (60) (62), with  $\text{Cl}_2$  in pres. of  $\text{Pb} + \text{PCl}_3$  (63), with  $\text{NOCl}$  at 150° (64) or 350° (65), with  $\text{NCl}_3$  (66), or with *ter*-butyl hypochlorite (3:7165) (62% yield (67)) see indic. refs.]

From benzyl alcohol. [For prepn. of  $\bar{C}$  from benzyl alcohol (1:6480) with  $\text{HCl}$  gas (68), with conc. aq.  $\text{HCl}$  at 60° (70–100% yield (69)) (70) in  $\text{C}_6\text{H}_6$  (study of kinetics at 60° (71)), with conc.  $\text{HCl} + \text{ZnCl}_2$  in cold (100% yield (72)), with  $\text{PCl}_3 + \text{ZnCl}_2$  (60% yield (72)), with  $\text{SOCl}_2$  (100% yield (73)) in  $\text{C}_6\text{H}_6$  (85% yield (72)) or in *N,N*-dimethylaniline (26% yield (72)), or with  $\text{AlCl}_3$  in pet. eth. above 40° (74) see indic. refs.]

From other miscellaneous sources. [For formn. of  $\bar{C}$  from benzyl chloroformate (3:9565) on bkg. (75) (76), from benzyl benzoate (1:4422) with 5 moles  $\text{SO}_2\text{Cl}_2$  (77), from dibenzyl ether (1:7640) or other benzyl ethers with  $\text{PCl}_3$  (78), from dibenzyl disulfide with excess  $\text{SO}_2\text{Cl}_2$  in  $\text{C}_6\text{H}_6$  at 37–39° (79), from benzylamine with  $\text{NOCl}$  in ether at  $-15^\circ$  (80) or with *aqua regia* (81), or from tetrabenzylhydrazine with conc.  $\text{HCl}$  on bkg. (82) see indic. refs.]

### CHEMICAL BEHAVIOR OF $\bar{C}$

Determination of  $\bar{C}$ . Many methods for detn. of  $\bar{C}$  have been employed and no complete listing can be given here; the following examples, however, may be helpful. [For detn. of  $\bar{C}$  by boilg. with alc.  $\text{AgNO}_3$  and weighing pptd.  $\text{AgCl}$  see (85) cf. (83); for detn. of  $\bar{C}$  in



$C_6H_6$  by addn. of excess standard  $AgNO_3$  in isopropyl alc., btg. several hrs., and excess  $AgNO_3$  titrated with standard aq.  $NaCl$  see (71); for methods of detn. of  $\bar{C}$  in pres. of benzal (di)chloride (3:6327) or benzotrichloride (3:6540) see (86) (87).]

Pyrolysis of  $\bar{C}$ . [ $\bar{C}$  on hoiling (34) (88) gradually dec. with evoln. of  $HCl$ . —  $\bar{C}$  over glowing Pt wire gives (89) (90) much stilbene (1:7250) accompanied (91) by small amounts of toluene (1:7405) and dibenzyl (1:7149).]

Resinification of  $\bar{C}$ .  $\bar{C}$  under the influence of various catalysts condenses with itself evolving  $HCl$  and yielding a material of composition  $(C_7H_6)_n$ ; this material is often (though incorrectly) designated as polymeric  $\bar{C}$ . Because of the indefinite character of the product and the voluminous and diffuse character of the literature, no exhaustive review will here be attempted. However, for extensive reviews of this reaction see (92) (93); for studies of catalysts for this type of reaction see also (94) (95) (96) (97).

Reduction of  $\bar{C}$ . [ $\bar{C}$  with  $H_2$  in pres. of  $Pd/BaCO_3$  (98) or  $Ni$  (99) in alc.  $KOH$  loses all its halogen as  $HCl$  (use in quant. detn.), but the corresp. org. reduction prod. has not been characterized. —  $\bar{C}$  with  $H_2$  in pres. of colloidal  $Pd$  in alc. gives (76% yield (100)) toluene (1:7405). —  $\bar{C}$  with  $EtOH + Zn$  dust on boilg. gives (101) cf. (102) toluene (1:7405) + benzyl ethyl ether (1:7530). —  $\bar{C}$  in  $EtOH/KOH$  with hydrazine hydrate in pres. of  $Pd$  boiled for 1 hr. gives (29% yield (103)) dibenzyl (1:7149); note that in conc. soln. only traces of dibenzyl are formed (103) cf. (104) and the principal prod. is *N,N*-dibenzylhydrazine [Beil. XV-533, XV<sub>1</sub>-(164)] accompanied by some benzyl ethyl ether (1:7530).]

Oxidation of  $\bar{C}$ .  $\bar{C}$  upon oxidn. yields either benzoic acid or benzaldehyde according to circumstances.

[ $\bar{C}$  with air at 160° over  $Ni$  cat. (105), with  $O_2$  in u.v. light (106), or with  $CrO_3/H_2SO_4$  at 95–98° for 1½ hrs. (note that  $\beta$ -chloroethylbenzene (3:8712) is stable under these conditions (107)) cf. (53), gives benzoic acid (1:0715). —  $\bar{C}$  with conc. aq. alk. nt 250–280° and at 300–500 lh./sq. in. press. gives (80–90% yield (108)) benzoic acid (1:0715).]

[ $\bar{C}$  with equimolal amt.  $SeO_2$  refluxed without solv. for 3 hrs. (109), with  $CrO_2Cl_2$  followed by aq. (110), with bot very dil.  $HNO_3$  (111) (112), with hot 14% aq.  $Ph(NO_2)_2$  (111), with boilg. aq.  $Ca(NO_3)_2$  (112), with boilg. aq.  $Na_2Cr_2O_7 + Na_2CO_3$  (113), with boilg. aq. or alc. hexamethylenetetramine (114) (115), with air at 160° over  $Ni$  cat. (105), or with steam + air at 360–480° over  $V_2O_5$  on pumice (116) (117) gives benzaldehyde (1:0195); naturally any over-oxidn. gives also some benzoic acid (1:0715).]

[Note that auto-ignition temp. of  $\bar{C}$  on  $Pt$  in air at ord. press. is 627° (118).]

Substitution of  $\bar{C}$ . Chlorination [ $\bar{C}$  with  $NOCl$  at 150° gives (64) benzal (di)chloride (3:6327). —  $\bar{C}$  with aq.  $PhCl_2 \cdot 2NH_4Cl$  on boilg. gives (119) benzal (di)chloride (3:6327) + benzotrichloride (3:6540). —  $\bar{C}$  with  $Cl_2$  in pres. of  $I_2$  at 30–40° gives (120) cf. (121) both *o*-chlorobenzyl chloride (3:6400) and *p*-chlorobenzyl chloride (3:0220). — Note that  $\bar{C}$  with  $Cl_2$  in sunlight (122) undergoes both substitution and addition and that only isolatable prod. was benzal (di)chloride hexachloride, m.p. 153°.]

Bromination. [ $\bar{C}$  with  $Br_2$  at 100° gives (123) cf. (124) a mixt. of benzyl bromide, benzal chlorobromide, and benzal (di) bromide. —  $\bar{C}$  with  $Br_2 + BeBr_2$  in ether gives (125) *p*-bromobenzyl bromide. —  $\bar{C}$  with  $Br_2$  in pres. of  $I_2$  gives (126) (127) a mixt. of *p*-bromobenzyl bromide and *p*-bromobenzyl chloride.]

Sulfonation. [Presumably because of facile hydrolysis or resinification of  $\bar{C}$  with conc.  $H_2SO_4$ , its direct sulfonation has not been reported. However, *p*-sulfobenzyl chloride ( $\omega$ -chlorotoluene-*p*-sulfonic acid) [Beil. XI<sub>1</sub>-(30)] has been prepd. (e.g., (128) (129)) from sodium salt of *p*-toluenesulfonic acid by chlorination.]

Nitration.  $\bar{C}$  on mononitration gives a mixt. of *o*-nitrobenzyl chloride [Beil. V-327, V<sub>1</sub>-(162), V<sub>2</sub>-(252)], m.p. 49–50° (130), 49.5° (17), 48–48.5° (131), 48–49° (132), 47.9° (133) (143), *m*-nitrobenzyl chloride [Beil. V-329, V<sub>1</sub>-(163), V<sub>2</sub>-(252)], m.p. 45–46° (130),

45.5° (17) (131) (134), 44.9° (143), 44.8° (133), and *p*-nitrobenzyl chloride [Beil. V-329,  $V_1$ -(163),  $V_2$ -(253)], cryst. from alc., m.p. 72.5° (17) (131) (134), 72.4° (133), 71-72° (130), 71.95° (143), 71° (53). — [For earlier studies of this mononitration of  $\bar{C}$  see (53) (135) (136) (137) (138) (139) and especially (140). — Subsequent studies of this mononitration have been primarily concerned with the proportion of isomers; e.g.,  $\bar{C}$  on mononitration with conc.  $HNO_3$  in acetic anhydride gives (133) 40.9% *o*-, 4.2% *m*-, and 54.9% *p*-nitrobenzyl chlorides (cf. (141) (142) (144)). — For thermal anal. of various mixtures of these three nitrobenzyl chlorides see (133) (143). — For study of rate of nitration of  $\bar{C}$  in nitrobenzene soln. at 16-18° see (145). Note that *p*-nitrobenzyl chloride is a useful reagent for characterization of organic acids by conversion to the corresp. *p*-nitrobenzyl esters (146) (147); for transformation of *p*-nitrobenzyl chloride to *p*-nitrobenzyl bromide in alc. NaBr see (147) cf. (148)]

[Direct polynitration of  $\bar{C}$  has not been reported; however, *p*-nitrobenzyl chloride on further nitration with  $HNO_3/H_2SO_4$  as directed (149) (150) gives 2,4-dinitrobenzyl chloride [Beil. V-344,  $V_2$ -(263)], tbs. from ether, m.p. 34° (150), 33-34° (149). — No other dinitrobenzyl chlorides and no trinitrobenzyl chlorides have been reported]

Hydrolysis of  $\bar{C}$ .  $\bar{C}$  on hydrolysis by various means gives benzyl alcohol (1:6480) and HCl.

[ $\bar{C}$  with aq. on protracted boilg. (151) (86) in sunlight (154), with steam + cat. at 550-850° (155) cf. (156), with boilg. nq.  $K_2CO_3$  (157) or alk.-earth carbonates at elev. temps. (158) (159), with hot nq. suspension of PbO (111), with boilg. nq.  $Na_2CO_3$ , NaOH, or their mixt. (160) (161), or with anhydrous formic acid (162) gives benzyl alcohol (1:6480). — For studies on kinetics of hydrolysis of  $\bar{C}$  in aq. (163) (169), in 95% EtOH at 30° and 40° (164) (165), in 50% acetone at 60° (166) cf. (167) (168) (170) (17), in dioxane (22), or in formic acid (170) see indic. refs.]

#### BEHAVIOR OF $\bar{C}$ WITH OTHER INORGANIC REACTANTS

With alkali sulfhydrylates. [ $\bar{C}$  with alc. KSH (171) (172) or aq. NaSH (173) (174) (175) gives (75% yield (172)) benzyl mercaptan [Beil. VI-453,  $VI_1$ -(224),  $VI_2$ -(427)], b.p. 194-195° (171), 99° at 32 mm (176), 75.8-76.2° at 10 mm. (11),  $D_4^{25} = 0.8097$  (176),  $n_D^{25} = 1.5729$  (176) (corresp. benzoate, m.p. 30° (177), 3,5-dinitrobenzoate, m.p. 119-120° (177), reaction prod. with 3-nitrophthalic anhydride, m.p. 136-137° (177), 2,4-dinitrophenyl thioether, m.p. 182.5° cor. (185)). Note that benzyl mercaptan with isotopic sulfur has been prepared (178) from  $\bar{C}$  via conversion to  $RMgCl$  and reaction with  $S^{34}$ .]

With alkali sulfides. [ $\bar{C}$  with alc.  $K_2S$  (171) or alc.  $Na_2S$  (179) gives (83% yield (179)) dibenzyl sulfide [Beil. VI-455,  $VI_1$ -(225),  $VI_2$ -(429)], tbs. from ether,  $CHCl_3$ , or alc., m.p. 49-50° (180), 49° (171) (179) (181) (corresp. sulfoxide [Beil. VI-456,  $VI_1$ -(226),  $VI_2$ -(429)], m.p. 135° (182), 132-134.6° (183), 132-133° (179); corresp. sulfone [Beil. VI-456,  $VI_1$ -(226),  $VI_2$ -(430)], m.p. 151° (184), 149.5-151° (183), 149.5-150° (179).]

With alkali polysulfides. [ $\bar{C}$  with alc.  $Na_2S_9H_2O + S$  (186) (189) in  $C_6H_6$  (187) cf. (188) gives dibenzyl disulfide [Beil. VI-465,  $VI_1$ -(229),  $VI_2$ -(437)], m.p. 74° (189), 72° (190), 71-72° (191), 70° (186) (corresp. disulfoxide [Beil. VI-466,  $VI_1$ -(230),  $VI_2$ -(438)], m.p. 108° (190) (192) cf. (209) (201) (210)].]

With salts of various sulfur acids. [ $\bar{C}$  with conc. aq.  $K_2SO_4$  (194) cf. (196) or  $Na_2SO_4$  (195) in aq. alc. at 37° (197) (for study of rate at 40° see (16)) or at 190-200° under press. (98% yield (198)), or  $\bar{C}$  with aq.  $Na_2SO_4/NaOH$  on boilg. (80% yield (199)) (192), gives corresp. salt of toluene- $\alpha$ -sulfonic acid (benzylsulfonic acid) [Beil. XI-116,  $XI_1$ -(32)]; for dimorphism of Na salt see (200) (corresp. sulfonyl chloride, m.p. 92-93° (201) (202), 92° (203); corresp. amide, m.p. 105° (203) (192), 104-105° (199), 102° (204); corresp. methyl ester, m.p. 61-62° (205)].]

[ $\bar{C}$  with  $\text{Na}_2\text{S}_2\text{O}_3$  on boil. in aq. alc. (206) or aq. (207) gives salt of *S*-benzylthiosulfuric acid [Beil. VI-439, VI<sub>1</sub>-(230)] (corresp. quaternary salt, viz., benzyl-dimethyl-phenyl-ammonium *S*-benzylthiosulfate, from metathesis of benzyl-dimethyl-phenyl-ammonium chloride with sodium *S*-benzylthiosulfate, has m.p.  $104^\circ$  (208)).]

With salts of other inorganic acids. [ $\bar{C}$  with NaI in acetone (211) (212) or abs. MeOH (213), or  $\bar{C}$  with KI in acetone (214) or EtOH (215), gives (90% yield (211)) benzyl iodide [Beil. V-314, V<sub>1</sub>-(157), V<sub>2</sub>-(241)], m.p.  $24^\circ$  (211) (212),  $27-30^\circ$  (213), b.p.  $97-98^\circ$  at 11 mm. (216),  $93^\circ$  at 10 mm. (214). — For study of rate of reaction of  $\bar{C}$  with KI in acetone at  $25^\circ$  (19) (20),  $30^\circ$  (19), and  $50^\circ$  (19), or with NaI or LiI in acetone at  $25^\circ$  or  $30^\circ$  (19), see indic. refs.]

[ $\bar{C}$  with powdered  $\text{AgNO}_3$  in dry ether 20 hrs. in cold, then at  $70-75^\circ$  for 5 hrs., gives (84% yield (219)) (220) benzyl nitrate [Beil. VI-439], explosive liquid, b.p.  $106^\circ$  at 20 mm. (219),  $100-101^\circ$  at 18 mm. (21),  $43^\circ$  at 0.5 mm. (220). — For study of kinetics of reaction of  $\bar{C}$  with solid  $\text{AgNO}_3$  (221) in pres. of inert diluents such as dry ether,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  (222) see indic. refs.; for study of kinetics of reaction of  $\bar{C}$  with  $\text{Hg}(\text{NO}_3)_2$  in aq. dioxane see (21).]

[ $\bar{C}$  with  $\text{AgNO}_2$  (223) (224) (231) or better mercurous nitrate (225) gives  $\omega$ -nitrotoluene (phenylnitromethane) [Beil. V-325, V<sub>1</sub>-(161), V<sub>2</sub>-(249)], b.p.  $225-227^\circ$  dec. (226) (227) cf. (228),  $141-142^\circ$  al. dec. at 35 mm. (226),  $135^\circ$  at 25 mm. (229),  $118-119^\circ$  at 16 mm. (230),  $110^\circ$  at 8 mm. (231),  $90-92^\circ$  at 3 mm. (232);  $D_4^{24.7} = 1.1540$  (233),  $D_D^{20} = 1.1598$  (226);  $n_D^{24.7} = 1.5285$  (233),  $n_D^{20} = 1.5323$  (226); note, however, that phenylnitromethane is best prepd. in a different way, viz., from benzyl cyanide with methyl nitrate and alc./NaOEt (50-55% yield (232)). — Note that the isomeric benzyl nitrite [Beil. VI-439], unstable oil, b.p.  $80-81^\circ$  at 35 mm. (234), has been reported from benzyl alcohol (1:6480) with aq.  $\text{NaNO}_2 + \text{H}_2\text{SO}_4$  (234).]

[ $\bar{C}$  with  $\text{NaN}_3$  in alc. refluxed 6 hrs. gives (90% yield (234))  $\omega$ -azidotoluene (benzyl azide) [Beil. V-350, V<sub>1</sub>-(174), V<sub>2</sub>-(274)], oil, insol. aq. and volatile with either steam or ether, b.p.  $108^\circ$  at 23 mm. (235),  $82.5^\circ$  at 16.5 mm. (234),  $74^\circ$  cor. at 11 mm. (236);  $D_4^{24.9} = 1.0655$  (237);  $n_D^{24.9} = 1.53414$  (237).]

[For behavior of  $\bar{C}$  with metallic cyanides see below under organic acids.]

With ammonia.  $\bar{C}$  with ammonia under various circumstances (see below) gives one (or more) of the following amines.

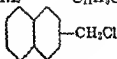
*Benzylamine* [Beil. XII-1013, XII<sub>1</sub>-(445)], liq. with faint characteristic odor, misc. with aq. alc. ether: b.p.  $184.5^\circ$  cor. at 760 mm. (238),  $184-186^\circ$  cor. at 745 mm. (239),  $184^\circ$  at 767 mm. (240),  $182^\circ$  at 749 mm. (226),  $181.5-182^\circ$  at 740 mm. (241),  $90^\circ$  at 12 mm. (242);  $D_4^{25} = 0.9812$  (243),  $D_4^{20} = 0.9822$  (244);  $n_D^{20} = 1.54015$  (226),  $n_D^{19.5} = 1.54406$  (244) (corresp.  $\bar{B}\cdot\text{HCl}$ , m.p.  $255.5-258^\circ$  (245),  $255-256^\circ$  rap. htg. (226),  $253^\circ$  (246);  $\bar{B}$   $\text{P}(\text{OH})_3$ , m.p.  $195-199^\circ$  (247),  $194^\circ$  (248);  $\bar{B}$ , 3,5-dinitrobenzoic acid, m.p.  $210.0^\circ$  cor. (249);  $\bar{B}$  2,4-dinitrobenzoic acid, m.p.  $199.1-200.1^\circ$  cor. (513);  $\bar{B}$ , *p*-toluenesulfonic acid, m.p.  $180.5-181.5^\circ$  u.c. (250),  $180^\circ$  (251)). — *Dibenzylamine* [Beil. XII-1035, XII<sub>1</sub>-(453)], oil, insol. aq., eas. sol. alc., ether; b.p.  $>300^\circ$  dec. (252),  $268-271^\circ$  cor. at 250 mm. (238),  $218-220^\circ$  at 60 mm. (253),  $215^\circ \pm 1^\circ$  at 39 mm. (254),  $186^\circ$  at 19 mm. (255),  $172^\circ$  at 14 mm. (256); f.p.  $-25.6^\circ$  (254);  $D_4^{25} = 1.024$  (255),  $1.019$  (257);  $D_4^{21.6} = 1.0256$  (244);  $n_D^{21.6} = 1.57432$  (244) (corresp.  $\bar{B}\cdot\text{HCl}$ , m.p.  $256^\circ$  (252),  $255.5^\circ$  (258);  $\bar{B}$ , *p*-toluenesulfonic acid, m.p.  $155.5-156.5^\circ$  u.c. (250)). — *Tribenzylamine* [Beil. XII-1038, XII<sub>1</sub>-(454)], solid, m.p.  $92^\circ$  (259) (260),  $91^\circ$  (256) (261) (262); b.p.  $218-222^\circ$  at 14 mm. (256),  $230^\circ$  at 13 mm. (259) (corresp.  $\bar{B}\cdot\text{HCl}$ , m.p.  $227-228^\circ$  (263),  $221^\circ$  (261);  $\bar{B}$ , *p*-toluenesulfonic acid, m.p.  $200.0-202.5^\circ$  u.c. (250)).

[For formn. of mixts. of benzylamine, dibenzylamine, and tribenzylamine (properties given in preceding paragraph) from reaction of  $\bar{C}$  with aq.  $\text{NH}_4\text{OH}$  at  $80^\circ$  for 8 days (264) or at  $125^\circ$  and 8 atm. press. (265) in pres. of cat. (266); from reaction of  $\bar{C}$  with alc.  $\text{NH}_3$  on

**3:0747 2-(CHLOROMETHYL)NAPHTHALENE**  
( $\beta$ -Naphthylmethyl chloride;  
 $\beta$ -menaphthyl chloride)

 $C_{11}H_9Cl$ 

Beil. V - 567

V<sub>1</sub>—V<sub>2</sub>-(464)

M.P. 48-40° (11)

B.P. 170° at 20 mm. (1)

48° (1)

168° at 20 mm. (2) (6)

47.8° (2)

162° at 15 mm. (1)

47-48° (3)

47° (4) (5) (6)

[See also 1-(chloromethyl)naphthalene (3:0250).]

Colorless cryst. from alc. (6) (5); loses HCl on attempted distn. at ord. press.

[For prepn. of  $\bar{C}$  from 2-methylnaphthalene (1:7605) with  $Cl_2$  in sunlight (5) (3) (6) and best at elevated temp., e.g. 220° (7) or even 250-280° (8) (53% yield (11)), see indic. refs.; from  $\beta$ -naphthylcarbinol [Beil. VI-668] (4) (2) with  $PCl_5$  (2) or with  $SOCl_2$  in toluene (4) see indic. refs.; from  $N$ -(benzoyl)- $\beta$ -naphthylmethylamine (1) or from  $N$ -(benzoyl)- $\beta$ -( $\beta$ -naphthylmethyl)amine (1) by hgt. with  $PCl_5$  see (1).]

$\bar{C}$  on oxidn. with aq.  $Pb(NO_3)_2$  soln. yields (6)  $\beta$ -naphthaldehyde (1:0036);  $\bar{C}$  on oxidn. with alk.  $KMnO_4$  yields (6)  $\beta$ -naphthoic acid (1:0800).

$\bar{C}$  on reductn. with Zn/Cu couple yields (2) 2-methylnaphthalene (1:7605).

[ $\bar{C}$  with excess Na in dry ether readily gives (8)  $\alpha,\beta$ -bis-(2-naphthylmethyl)ethane, m.p. 182° (9) (picrate, m.p. 198° (9)).] — [For study of reactn. of  $\bar{C}$  with 1-(chloromethyl)-naphthalene (3:0250) +  $AlCl_3$  in  $CS_2$  see (7).]

[ $\bar{C}$  with Mg in dry ether + trace  $C_2H_5I$  gives corresp.  $\beta$ - $C_{10}H_7CH_2MgCl$ , but reactn. is capricious and requires pure  $\bar{C}$  (4), the  $RMgCl$  cpd. with  $AcCl$  in ether does not follow a normal course but gives instead 1,3-di-( $\beta$ -naphthyl)-2-methylpropene-1, cryst. from  $AcOH$ , m.p. 184-185° (4).]

[For study of reactn. of  $\bar{C}$  with ethyl acetoacetate +  $NaOEt$  in abs. alc. giving (83% yield) ethyl  $\alpha$ -( $\beta$ -naphthylmethyl)acetoacetate see (10).]

$\bar{C}$  with aq. at 100° for 1½ hrs. is 17% hydrolyzed (1).

[ $\bar{C}$  with large excess of conc.  $C_6H_6$  soln. of dimethylamine htd. in s.t. at 100° for 10 hrs. yields (1)  $N,N$ -dimethyl- $\beta$ -naphthylmethylamine.]

3:0747 (1) von Braun, Moldaske, *Ber.* 56, 2168-2171 (1923). (2) Sah, *Rec. trav. chim.* 59, 461-470 (1910), *C.A.* 35, 4763 (1911). (3) Achmatowicz, Lundenfeld, *Roczniki Chem.* 18, 69-74 (1938); *Cent.* 1939, II 359 (4) Campbell, Anderson, Gilmore, *J. Chem. Soc.* 1940, 820. (5) Scherle, *Ber.* 17, 1529 (1884). (6) Schulze, *Ber.* 17, 1529 (1884). (7) Clar, Lombardi, *Gazz. chim. ital.* 62, 542-544 (1932), *C.A.* 27, 81 (1933). (8) Clar, Wallenstein, *Ber.* 64, 2080, 2082 (1931). (9) Friedman, *Ber.* 49, 1354-1355 (1916). (10) Sempron, *Gazz. chim. ital.* 63, 263-266 (1938).

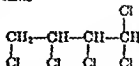
(11) Tarbell, Fukushima, Dam, *J. Am. Chem. Soc.* 67, 108 (1945).

**3:0750 1,1,2,3,4-PENTACHLOROBUTANE**

(Solid diastereoisomer)

(1,2,3,4,4-Pentachlorobutane  
(solid diastereoisomer)) $C_4HCl_5$ 

Beil. S.N. 10



M.P. 49° (1) B.P. 230°

(1)  $D^{25}_D = 1.530$  (2)  $n^{25}_D = 1.5065$  (2)

48° (2)

105-107° at 13 mm. (1)

102° at 11 mm. (2)

[See also liquid diastereoisomer (3:0063).]

gives (yields: 92% (329), 85% (212)) benzylamine (for constants see above under behavior of  $\bar{C}$  with  $NH_3$ ) as hydrochloride;  $RMgCl$  with  $BrNH_2$  gives (63% yield (330)) benzylamine. —  $RMgCl$  with  $NCl_3$  gives (331) both benzylamine (32% yield) and dibenzylamine (7% yield). —  $RMgCl$  with  $SiF_4$  gives (336)  $(C_6H_5.CH_2)_3SiF$ , m.p.  $79^\circ$ , accompanied by some  $(C_6H_5.CH_2)_4Si$ , m.p.  $127.5^\circ$ ; the latter is also obtd. (20.7% yield (337)) from  $RMgCl$  with  $Na_2SiF_6$ .]

$RMgCl$  with organic reactants frequently (but not invariably) leads to products derived from *o*-tolyl  $MgCl$  and/or *p*-tolyl  $MgCl$ : for reviews on and studies of this rearr. of  $RMgCl$  see (332) (333) (334) (335). —  $RMgCl$  shows little if any tendency to act as a reducing agent in Grignard additions; for review of reducing action of many Grignard reagents (including  $C_6H_5.CH_2MgCl$ ) see (338).

[ $RMgCl$  with  $CO$  at  $120^\circ$  under press. gives (60% yield (339)) 1,3-diphenylpropene-1 [Beil. V-643,  $V_1$ -(310),  $V_2$ -(552)]. —  $RMgCl$  with  $CO_2$  gives (yields: 75–76% (310), 62.7% (335), 60% (340), 51% (318), 40% (333)) phenylacetic acid (1:0665).]

[ $RMgCl$  with trioxymethylene gives (50–55% yield (341)) (342) (343) *o*-tolylcarbinol (1:5922) (note rearr.), but  $RMgCl$  with nectaldehyde (as paraldehyde) gives (343) (335) the expected benzyl-methyl-carbinol [Beil. VI-503,  $VI_1$ -(251),  $VI_2$ -(472)]. —  $RMgCl$  with benzaldehyde gives according to conditions various prods. including benzyl-phenyl-carbinol (1:5958) (78% yield (344)) (345) (346), stilbene (1:7250) (25–35% yield (316)), and other products.]

[ $RMgBr$  with acetone gives (347) (343) benzyl-dimethyl-carbinol (1:5910). —  $RMgCl$  gives with diphenylketone (85% yield (349)) (348) benzyl-diphenyl-carbinol [Beil. VI-721,  $VI_1$ -(354),  $VI_2$ -(696)] easily dehydrated to (54–59% overall yield (316))  $\alpha,\alpha,\beta$ -triphenylethylene [Beil. V-722,  $V_1$ -(355),  $V_2$ -(630)].]

[ $RMgCl$  with  $ClCH_2OCH_3$  (3:7035) according to circumstances gives either or both the "normal" prod. (350) (351) methyl  $\beta$ -phenylethyl ether [Beil. VI-479,  $VI_1$ -(238),  $VI_2$ -(449)] and the "abnormal" prod. (352) (353) methyl *o*-tolylcarbinyl ether [Beil. VI-484]. —  $RMgCl$  with  $ClCH_2O.CH_2CH_3$  (3:7195) according to circumstances gives either or both the "normal" prod. (354) ethyl  $\beta$ -phenylethyl ether [Beil.  $VI_1$ -(450)] or the "abnormal" products (352) (352) ethyl *o*-tolyl ether [Beil. VI-484] and ethyl *p*-tolyl ether [Beil. VI-498].]

[ $RMgCl$  with methyl chloroformate (3:5075) gives some "abnormal" prod. (333). —  $RMgCl$  with ethyl chloroformate (3:7295) gives not only the "normal" tribenzylcarbinol [Beil. VI-723,  $VI_1$ -(356)] (355) and ethyl phenylacetate (1:3872) but also "abnormal" products (332) (333).]

[ $RMgCl$  with acetyl chloride (3:7065) gives (yields: 24% (333), 18% (335)) (332) the "abnormal" product, methyl *o*-tolyl ketone (*o*-methylacetophenone) (1:5224). —  $RMgCl$  with benzoyl chloride (3:6240) gives (333) the "abnormal" product, phenyl *o*-tolyl ketone [Beil. VII-439,  $VII_1$ -(234)].]

[ $RMgCl$  with benzenesulfonyl chloride gives (356) (357) benzyl phenyl sulfone [Beil. VI-455,  $VI_2$ -(428)] (2.9% yield (356)) cf. (357) and  $\bar{C}$  (60% yield (356))]

$RMgCl$  with alkyl *p*-toluenesulfonates gives hydrocarbons. — [E.g.,  $RMgCl$  with methyl *p*-toluenesulfonate gives (40.9% yield (358)) ethylbenzene (1:7410), with ethyl *p*-toluenesulfonate (358) or diethyl sulfate (359) gives (yields: 100% (359), 38.3% (358)) *n*-propylbenzene (1:7450), with *n*-propyl *p*-toluenesulfonate gives (35.6% yield (358)) *n*-butylbenzene (1:7515), with *n*-butyl *p*-toluenesulfonate gives (yields: 67% (361), 50–59% (360), 24.6% (358)) *n*-amylbenzene (1:7549). —  $RMgCl$  with  $\gamma$ -chloro-*n*-propyl *p*-toluenesulfonate gives (42–50% yield (362))  $\omega$ -chloro-*n*-butylbenzene ( $\delta$ -phenyl-*n*-butyl chloride) [Beil.  $V_1$ -(201),  $V_2$ -(317)].]

stdg. several days (268) (269) (270) or in s.t. at  $100^\circ$  (256) (267), with  $\text{NH}_3$  in conc. aq. phenol in s.t. at  $100^\circ$  for 18 hrs. (271), with liq.  $\text{NH}_3$  for 24 hrs. (256), or with 5 moles aq.  $(\text{NH}_4)_2\text{CO}_3$  for 5-6 hrs. at  $85-110^\circ$  (160) see indic. refs.]

[For formn. of benzylamine from reaction of  $\bar{\text{C}}$  with K phthalimide at  $170-180^\circ$  followed by hydrolysis of the *N*-benzylphthalimide (see below under  $\bar{\text{C}}$ 's) with fuming  $\text{HCl}$  at  $200^\circ$  for 2 hrs (272) cf. (273) (274), with silver cyanate followed by hydrolysis with alkali (275) (276) cf. (268) (277), with acetamide followed by hydrolysis with alc.  $\text{KOH}$  (278), or with hexamethylenetetramine followed by hydrolysis with alc.  $\text{HCl}$  (279) see indic. refs.]

[For formn. of tribenzylamine from reaction of  $\bar{\text{C}}$  with  $\text{NaNH}_2$  at  $120^\circ$  for 24 hrs. see (261) (280)]

With hydroxylamine.  $[\bar{\text{C}}$  with  $\text{NH}_2\text{OH} \cdot \text{HCl} + \text{Na}_2\text{CO}_3$  in aq. alc. under reflux gives (281) (282) (283) (284) *N,N*-dibenzylhydroxylamine [Beil. XV-19, XV<sub>1</sub>-(9)], m.p.  $124^\circ$  (284),  $123-124^\circ$  (285),  $123^\circ$  (281); note that the isomeric *O,N*-dibenzylhydroxylamine [Beil. XV-21], oil, b.p.  $145-146^\circ$  at 3 mm. (286), is obt'd. indirectly. —  $\bar{\text{C}}$  with acetone oxime refluxed in 75%  $\text{AcOH}$  gives (287) (as the hydrochloride) *N*-benzylhydroxylamine [Beil. XV-17, XV<sub>1</sub>-(8)], m.p.  $57^\circ$  (288),  $56-58^\circ$  (289) ( $\bar{\text{B}} \cdot \text{HCl}$ , m.p.  $110^\circ$  (288)). — Various other benzylated hydroxylamines cannot be discussed here.]

With hydrazine.  $[\bar{\text{C}}$  with alc. 50% hydrazine hydrate under reflux gives (290) *N,N*-dibenzylhydrazine [Beil. XV-533, XV<sub>1</sub>-(164)], m.p.  $65^\circ$  ( $\bar{\text{B}} \cdot \text{HCl}$ , m.p.  $202^\circ$  (292),  $200^\circ$  (290)); note that the isomeric *N',N'*-dibenzylhydrazine [Beil. XV-534, XV<sub>1</sub>-(166)], m.p.  $47^\circ$  (291) ( $\bar{\text{B}} \cdot \text{HCl}$ , m.p.  $225^\circ$  (293)), is prep'd. indirectly. — Various other benzylated hydrazines cannot be discussed here.]

With metals. Sodium  $[\bar{\text{C}}$  with  $\text{Na}$  at  $30^\circ$  on stdg. gives (294) encrustation of  $\text{NaCH}_2 \cdot \text{C}_6\text{H}_5$  [Beil. XVI<sub>1</sub>-(589)]; the solid is wine red within 5 hrs., red-violet in 12 hrs., blue-violet in 36 hrs., and finally blue-black; and the sodium benzyl can be isolated as a blue-violet solid stable in air (294) —  $\bar{\text{C}}$  with  $\text{Na}$  at  $100^\circ$  (295) in a mixt. of  $\text{C}_6\text{H}_6$  and toluene (296) or in toluene (297) gives dibenzyl (1:7149). —  $\bar{\text{C}}$  with  $\text{Na}$  in liq.  $\text{NH}_3$  loses its halogen quantitatively (298) giving (50% yield (299)) dibenzyl (1:7149) accompanied by toluene and other products. — For study of free benzyl radical from  $\bar{\text{C}}$  with  $\text{Na}$  vapor in helium see (302)]

$[\bar{\text{C}}$  with  $\text{Cu}$  powder in s.t. at  $150-160^\circ$  for 12 hrs (300), or  $\bar{\text{C}}$  with  $\text{Al}$  powder (pretreated with  $\text{H}_2$  at  $500^\circ$ ) refluxed at  $200^\circ$  for 1 hr (301), gives (60% yield (301)) dibenzyl (1:7149).]

Magnesium  $[\bar{\text{C}}$  as vapor passed over htd.  $\text{Mg}$  gives (303) magnesium allylide which with aq. yields methylacetylene ("allylene").]

$[\bar{\text{C}}$  with  $\text{Mg}$  in dry ether gives (304) (305) (306)  $\text{C}_6\text{H}_5 \cdot \text{CH}_2\text{MgCl}$ : for study of optimum conditions (311) giving yields of 94.25% (307), 93.2% (308), 91.0-94.1% (309), 90.7-91.2% (310) see indic. refs.; for study of effect of nature of  $\text{Mg}$  (312), of use of ether/hydrocarbon mixts. as solvent (313), of stability toward long holdg. in ether or ether/benzene (314) see indic. refs., for further examples of practical prepn. of  $\text{C}_6\text{H}_5 \cdot \text{CH}_2\text{MgCl}$  see (315) (316). — Note that some dibenzyl (1:7149) (e.g., 9.4% (317)) and di-*p*-tolyl (4,4'-dimethylbiphenyl) (318) are also formed and the yield of dibenzyl is greatly increased in pres. of cat. such as  $\text{CuCl}_2$ ,  $\text{HgBr}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeBr}_3$  (319), or  $\text{MoCl}_5$  (320).]

An exhaustive treatment of the behavior of  $\text{C}_6\text{H}_5 \cdot \text{CH}_2\text{MgCl}$  (hereafter called  $\text{RMgCl}$ ) is far beyond the scope of this book, but the following examples will be useful and will serve as lead references; for further examples see Beil. XVI-939, XVI<sub>1</sub>-(554) and subsequent literature.

$[\text{RMgCl}$  with  $\text{O}_2$  gives (80% yield (321)) cf. (322) benzyl alcohol (1:6480). —  $\text{RMgCl}$  (1 mole) gives (84% yield (323)) (324) (325)  $\text{C}_6\text{H}_5 \cdot \text{CH}_2\text{HgCl}$ , m.p.  $104^\circ$  (323) (324) (326), but excess  $\text{RMgCl}$  with  $\text{HgCl}_2$  gives (326) (325) (327) dibenzyl mercury, m.p.  $111^\circ$  (326). —  $\text{RMgCl}$  with  $\text{SbCl}_5$  gives (328) tribenzylstilbene, m.p.  $107-108^\circ$ . —  $\text{RMgCl}$  with  $\text{ClNH}_2$

[ $\bar{C}$  with benzyl alc./ $\text{NaOCH}_2\text{C}_6\text{H}_5$  in ether (415), with solid KOH at 180–200° (416), with conc. aq. NaOH at 90–120° (416), or with K benzylate in liq.  $\text{NH}_3$  (408) gives dibenzyl ether (1:7640).]

With phenols (or phenolates).  $\bar{C}$  with phenols may react either with phenolic or nuclear hydrogen giving respectively benzyl aryl ethers or benzylated phenols; moreover, the former may, under appropriate conditions, be rearranged to the latter; examples of all these types of reaction are included below.

[ $\bar{C}$  with K phenolate (111) (418) or Na phenolate (417) in boilg. alc., or  $\bar{C}$  with phenol in boilg. alc. NaOMe or NaOEt (419) (420), boilg. aq. NaOH (160) (421), or boilg. acetone +  $\text{K}_2\text{CO}_3$  (422) gives (73% yield (421)) benzyl phenyl ether [Beil. VI-432,  $\text{VI}_1$ -(220),  $\text{VI}_2$ -(411)], m.p. 39° (418) (420) (421) (422), 38–39° (401); b.p. 286–287° (401), 286–288° (419), 178–179° at 35 mm. (422), 124–125° at 4 mm. (417). — Note that although this prod. is completely stable to distn. (419) yet on htg. with  $\text{ZnCl}_2$  or in dry HCl as directed (421) it undergoes rearr. (accompanied by some cleavage) giving 2-benzylphenol (1:1431), 4-benzylphenol (1:1485), 2,4-dibenzylphenol (see below), and other prods.]

$\bar{C}$  under suitable conditions also effects nuclear benzylation of phenol yielding a mixt. of *o*-benzylphenol (1:1431) and *p*-benzylphenol (1:1485) (the latter usually predominating) accompanied by polybenzylphenols and other products. [E.g.,  $\bar{C}$  with phenol (1:1420) directly at 125° (423) or 150–180° (160), or in pres. of Cu powder at 115–120° (160), Ce at 120–130° (424), Ti (393),  $\text{AlCl}_3$  in pet. ether (425), Zn at room temp. (426) (427) (428) (429) in solvent media such as  $\text{C}_6\text{H}_6$ , toluene,  $\text{CHCl}_3$ , or EtOH (430),  $\text{ZnCl}_2$  on warming (421) (431) (432), 38% HCl in s.t. at 100° (421),  $\text{P}_2\text{O}_5$  (434) or  $\text{PCl}_5$  (435) in toluene at 130–135°, or  $\bar{C}$  with Na phenolate (or phenol + Na) in dry toluene (419) (436) (437) gives *o*-benzylphenol + *p*-benzylphenol (accompanied by other products). — For sepn. of the two benzylphenols by formn. of Na salt of latter in toluene see (438).]

Other phenols, cresols, naphthols, etc., behave analogously but cannot be discussed here.

With phenol ethers. With phenol ethers (where no phenolic H atom is available for reaction)  $\bar{C}$  effects nuclear benzylation. [E.g.,  $\bar{C}$  with methyl phenyl ether (anisole) (1:7445) refluxed 2–3 hrs. (391), or in pres. of Zn (439), Ti (393), Ce (424), W (365),  $\text{AlCl}_3$  (440), or  $\text{ZnCl}_2$  + dry HCl (421) gives (yields: 63% (393), 57% (424), 52.9% (365)) *p*-benzylanisole [Beil. VI-676,  $\text{VI}_1$ -(325),  $\text{VI}_2$ -(630)], b.p. 305–308° (425), 191–193° at 38 mm. (391), 172–174° at 10 mm. (421), 157–158° at 8 mm. (411), 133–135° at 4 mm. (425); m.p. 20–21° (441).]

[ $\bar{C}$  with phenetole (1:7485) in pres. of Ti (393), U (365), or Ce (424) as directed gives (yields: 76% (393), 80% (365), 88% (424)) *p*-benzylphenetole [Beil. VI-676,  $\text{VI}_2$ -(630)], b.p. 317° (442), 315–317° (425), 217° at 37 mm. (442), 203° at 12 mm. (442), 171–173° at 12 mm. (425).]

With organic acids (or their salts). *KCN or NaCN*. [ $\bar{C}$  with alc. KCN (443) (444) (445) (446) in pres. of CuCN and in u.v. light (447), or  $\bar{C}$  with aq. alc. NaCN (160) (448), gives (yields: 80–90% (448), 70–76% (447), 70% (160)) benzyl cyanide ( $\alpha$ -tolunitrile) (phenylacetoneitrile) [Beil. IX-441,  $\text{IX}_1$ -(176)], b.p. 233–234° cor. (3), 231–232° at 755 mm. (449), 135–140° at 38 mm. (448), 118–119° at 20 mm. (450), 107–107.4° at 12 mm. (18); f.p. –24.6° (26), –26.5° (451);  $D_4^{25} = 1.0125$  (452),  $D_4^{20} = 1.0176$  (453), 1.0157 (454);  $n_D^{25} = 1.52105$  (455),  $n_D^{20} = 1.52422$  (453); for removal from this prod. of traces of benzyl isocyanide with aq.  $\text{H}_2\text{SO}_4$  at 60° see (456).]

With salts of aliphatic acids. [ $\bar{C}$  with Na formate + anhydrous formic acid in s.t. at 140° (402) gives benzyl formate (1:3596) q.v.]

[ $\bar{C}$  with KOAc in alc. (443) (457) (460) or benzyl acetate itself (458), or  $\bar{C}$  with  $\text{Pb}(\text{OAc})_2$  in AcOH (459), or  $\bar{C}$  with NaOAc in AcOH (461) cf. (160) or aq. at 115° (160), gives (80% yield (160)) benzyl acetate (1:3751) q.v.; for study of kinetics see (22).]

BEHAVIOR OF  $\bar{C}$  WITH ORGANIC REACTANTS

With hydrocarbons.  $\bar{C}$  with benzene (1:7400) in pres. of widely varied condensing agts. gives diphenylmethane (1:7120), frequently accompanied by *o*-dibenzylbenzene [Beil. V-710,  $V_1$ -(351),  $V_2$ -(621)], m.p. 78-79°, and by *p*-dibenzylbenzene [Beil. V-711,  $V_1$ -(351),  $V_2$ -(621)], m.p. 86°. — [E.g.,  $\bar{C}$  with benzene (1:7400) in pres. of Zn dust (363) (369), Cr powder (364), uranium dust at 100° for 4 hrs. (365), Al powder (preheated in  $H_2$  at 500°) (301), Ti (393), Al/Hg (366) (367), Al +  $HgCl_2$  (368), Al + HCl (368),  $AlCl_3$  (369) (370),  $AlCl_3$ /nitrobenzene cpd. at 30° (372),  $NaCl/AlCl_3$  at 15-20° (373),  $BeCl_2$  at 100° for 6 hrs. (374),  $TiCl_4$  (375),  $ZrCl_4$  (376),  $SnCl_4$ /diethyl etherate (377),  $TiCl_3$  (378), iron pyrites (37),  $Ag_2SO_4$  (379), silver methionate (neutral silver salt of methanedisulfonic acid) (379),  $P_2O_5$  (380), or HF in Cu bomb nt 100° for 15 hrs (381)] gives (yields: 60-63% (368), 60% (372) (374), 56% (381), 52% (373), 49.5-52.5% (366), 40% (365), 38% (301), 35% (375), 30% (376), 22% (363)) diphenylmethane (1:7120).]

[ $\bar{C}$  with toluene (1:7405) in pres. of Zn dust (382) cf. (383) (384), Ti (393),  $AlCl_3$  (369) (370) cf. (385) (386) (371), Al/Hg (367),  $FeCl_3$  (385) (386),  $BeCl_2$  at 110-125° (374), or  $MeMgI$  (387) gives *p*-benzyltoluene [Beil. V-607,  $V_1$ -(286),  $V_2$ -(511)], b.p. 279°.]

[ $\bar{C}$  with *m*-xylene (1:7420) in pres. of Zn dust (388), finely divided Cu (389), or  $BeCl_2$  at 130-140° (374) gives (78.6% yield (384)) phenyl-*m*-xylyl-methane [Beil. V-615,  $V_1$ -(289),  $V_2$ -(518)], b.p. 295-296° cor. (388) (389).]

[ $\bar{C}$  with mesitylene (1:7455) refluxed 60 hrs. without cat. (391), or in pres. of  $AlCl_3$  (390) at 98-100°, or  $BeCl_2$  at 140-160° (374), gives (78% yield (374)) benzylmesitylene (phenyl-2,4,6-trimethylphenyl-methane) [Beil. V-619], m.p. 36-37° (390), 36° (374).]

[ $\bar{C}$  with biphenyl (1:7175) refluxed 3 hrs. without cat. (391), or in pres. of Zn dust at 100° (392), or of Ti (393) gives 4-benzylbiphenyl [Beil. V-708,  $V_2$ -(618)], m.p. 85° (392) (391).]

[ $\bar{C}$  with naphthalene (1:7200) refluxed 3 hrs. without cat. (391), or in pres. of Zn dust (394) (395),  $ZnCl_2$  (396) at not over 125° (397),  $AlCl_3$  (396) (398), Ti (393), or  $P_2O_5$  at 200° (380) gives mainly 1-benzyl-naphthalene [Beil. V-689,  $V_1$ -(341),  $V_2$ -(604)], m.p. 59° (corresp. picric acid addn. cpd., m.p. 100-101° (396) (400)), accompanied by some 2-benzyl-naphthalene [Beil. V-690], m.p. 55-55.5° (398), 55.5° (399) (corresp. picric acid addn. cpd., m.p. 93° (396) (400)). — Note that using  $ZnCl_2$  little 2-benzyl-naphthalene is formed (398), also that polybenzylation may occur (399).]

With alcohols (or alcoholates). [ $\bar{C}$  with  $MeOH/KOH$  (401) or with  $MeOH/NaOMe$  (403) in s.t. at 120° (402) gives benzyl methyl ether (1:7475), b.p. 170-171° cor. (403), 170.5° cor. at 760 mm. (3), 170-171° at 759 mm. (377), 170.2-172.2° at 760 mm (404);  $D_4^{25} = 0.9745$  (405), 0.9594 (403),  $D_4^{20} = 0.9649$  (403);  $n_D^{25} = 1.4983$  (403),  $n_D^{20} = 1.5031$  (405), 1.5008 (403) (corresp. picrate, m.p. 115-116° u.c. (406)). —  $\bar{C}$  with  $EtOH/KOH$  (401),  $EtOH/NaOEt$  (403) (377) (407),  $EtOH/LaOEt$  (407), or  $KOEt/liq. NH_3$  (408) gives (yields: 81% (408), 63-77% (407)) benzyl ethyl ether (1:7530); b.p. 184.7-185.2° at 761 mm. (377), 184-186° cor. (403);  $D_4^{25} = 0.9446$  (403),  $D_4^{20} = 0.9490$  (409), 0.9478 (403);  $n_D^{25} = 1.4934$  (403),  $n_D^{20} = 1.4958$  (403), 1.4955 (409). — For studies of rate of reaction of  $\bar{C}$  with  $EtOH$  (410) (411) or with  $EtOH/NaOEt$  (412) see indic. refs.]

[ $\bar{C}$  with *n*- $PrOH/NaO-n-Pr$  gives (90-93% yield (413) (403)) benzyl *n*-propyl ether [Beil. VI-431,  $V_1$ -(219),  $V_2$ -(410)], b.p. 200-202° cor. (403), 68° at 9 mm. (413);  $D_4^{25} = 0.9480$  (403),  $D_4^{20} = 0.9535$  (403) cf. (413);  $n_D^{25} = 1.4932$  (403),  $n_D^{20} = 1.4953$  (403), 1.4905 (413); for study of rate at 50.6° see (414). —  $\bar{C}$  with *iso*- $PrOH/NaOisoPr$  gives (403) benzyl isopropyl ether, h.p. 192-194° cor.;  $D_4^{25} = 0.9403$ ,  $D_4^{20} = 0.9457$ ;  $n_D^{25} = 1.4876$ ,  $n_D^{20} = 1.4900$  (403).]

[For corresp. prepn. and constants for benzyl *n*-butyl ether (403) (417), benzyl *sec*-butyl ether (417), benzyl isobutyl ether (403), and benzyl isomyl ether (403) see indic. refs.]



[ $\bar{C}$  with  $C_2H_5NH_2$  in 33% aq. soln. with some alc. in s.t. at  $110^\circ$  gives (558) *N*-ethylbenzylamine [Beil. XII-1020, XII<sub>1</sub>-(448)], oil, spar. sol. aq., b.p.  $199^\circ$  (589),  $198^\circ$  at 750 mm. (550),  $194^\circ$  cor. (558),  $191$ – $194^\circ$  u.c. at 740 mm. (548);  $D_{15}^{25} = 0.9350$  (552) ( $\bar{B}$ .P.KOH, m.p.  $122$ – $123^\circ$  (559)), accompanied by *N*-ethyldibenzylamine [Beil. XII-1036], b.p.  $306^\circ$  cor. (558).]

*With aromatic primary amines.* [ $\bar{C}$  (1 mole) with aniline (2 moles) in s.t. at  $160^\circ$  for 24 hrs. (502), or htd. in open vessel at  $140^\circ$  (503), or in pres. of  $I_2$  at  $50^\circ$  (504), in alc. (505) or aq.  $Na_2CO_3$  (160), or  $\bar{C}$  (1 mole) with aniline (4 moles) in aq.  $NaHCO_3$  at  $90$ – $95^\circ$  (506), or  $\bar{C}$  with sodium anilide (from aniline + Na +  $Cu_2O$ ) nt  $30$ – $100^\circ$  under press., (507) gives (yields: 85–87% (506), 56% (160), 49% (504)) *N*-benzylaniline (*N*-phenylbenzylamine) [Beil. XII-1023, XII<sub>1</sub>-(449)], m.p.  $39^\circ$  (508),  $37$ – $38^\circ$  (509),  $37^\circ$  (510),  $36.5$ – $36.8^\circ$  cor. (503),  $36.5^\circ$  (511),  $36^\circ$  (506) (512); b.p.  $306$ – $307^\circ$  at 759 mm. (509),  $201$ – $203^\circ$  at 37 mm. (510),  $178$ – $180^\circ$  at 12 mm. (506),  $171.5^\circ$  at 10 mm. (508);  $D_4^{25} = 1.0298$  (508);  $n_D^{25} = 1.59562$  (508) ( $\bar{B}$ .HCl, m.p.  $214$ – $216^\circ$  (509),  $\bar{B}$ .3,5-dinitrobenzoic acid, m.p.  $133.0^\circ$  cor. (249),  $\bar{B}$ .2,4-dinitrobenzoic acid, m.p.  $121.4$ – $122.2^\circ$  cor. (513),  $\bar{B}$ .*p*-toluenesulfonic acid, m.p.  $148.3$ – $148.8^\circ$  cor. (250)); for method of sepn. of *N*-benzylaniline from *N,N*-dibenzylaniline (below) by reactn. with phthalic anhydride (1:0725) see (514). — For studies of kinetics of reaction of  $\bar{C}$  with aniline in MeOH nt  $35^\circ$  and  $45^\circ$  (515) or in EtOH at  $35^\circ$ ,  $40^\circ$ , and  $45^\circ$  (516) cf. (4) see indic. refs.; for study of rearr. of *N*-benzylaniline to *p*-aminodiphenylmethane see (517)]

[ $\bar{C}$  with aniline on htg. cf. (503) (508) in pres. of NaOH at  $100^\circ$  (518), anhydrous NaOAc +  $I_2$  at  $97^\circ$  (504),  $NaNH_2$  + Cu powder (519), benzyl alc. (520), or aq.  $Na_2CO_3$  (160) gives *N,N*-dibenzylaniline (*N*-phenyldibenzylamine) [Beil. XII-1037, XII<sub>1</sub>-(453)], m.p.  $71$ – $72^\circ$  (521),  $70^\circ$  (522),  $69.5^\circ$  (508),  $69^\circ$  (520),  $67^\circ$  (518); b.p.  $226^\circ$  at 10 mm. (508);  $D_4^{25} = 1.04436$ ;  $n_D^{20} = 1.60647$  (508) ( $\bar{B}$ .HCl, pr. with 1  $H_2O$  from alc. (518), but m.p. unreported;  $\bar{B}$ .P.KOH, m.p.  $131$ – $132^\circ$  dec. (518);  $\bar{B}$ .3,5-dinitrobenzoic acid gives no cpd. (249);  $\bar{B}$ .2,4-dinitrobenzoic acid gives no cpd. (513);  $\bar{B}$ .*p*-toluenesulfonic acid is oil (250);  $2\bar{B}$ .1,3,5-trinitrobenzene, m.p.  $86$ – $87^\circ$  (523)). — For study of rearr. of *N,N*-dibenzylaniline hydrochloride to *p*-aminodiphenylmethane, 2,4-dibenzylaniline, and 2,4,6-tribenzylaniline see (524).]

$\bar{C}$  with other aromatic primary amines behaves similarly but cannot be detailed here; however, for a number of cases see (508).

*With aliphatic secondary amines.* [ $\bar{C}$  with  $(CH_3)_2NH$  in abs. alc. on stdg. (560) or under reflux (546) (561), or in  $C_6H_6$  at  $40$ – $50^\circ$  for 2 days (562), gives (80% yield (561)) *N,N*-dimethylbenzylamine [Beil. XII-1019, XII<sub>1</sub>-(448)], oil, fairly sol. cold but less sol. hot aq., b.p.  $183$ – $184^\circ$  cor. at 765.3 mm. (560),  $180$ – $181^\circ$  nt 749 mm. (540),  $178$ – $179^\circ$  cor. (563),  $177.8$ – $178.2^\circ$  cor. at 766 mm. (561),  $178^\circ$  u.c. (562),  $98$ – $99^\circ$  at 24 mm. (564),  $83.5$ – $85.5^\circ$  at 21 mm. (565),  $66$ – $67^\circ$  at 15 mm. (566),  $n_D^{20} = 1.5157$  (564) ( $\bar{B}$ .HCl, m.p.  $175^\circ$  (562) cf. (566);  $\bar{B}$ .P.KOH, m.p.  $94^\circ$  (532),  $94$ – $95^\circ$  (559)).]

[ $\bar{C}$  with  $(C_2H_5)_2NH$  in s.t. at  $100^\circ$  gives (567) (568) *N,N*-diethylbenzylamine [Beil. XII-1021, XII<sub>1</sub>-(448)], oil, spar. sol. aq., b.p.  $212^\circ$  (569),  $211$ – $212^\circ$  (568) cor. (567),  $209^\circ$  (570) at 755 mm. (551),  $96$ – $98^\circ$  at 17 mm. (564),  $94^\circ$  at 15 mm. (555) ( $\bar{B}$ .P.KOH, m.p.  $120$ – $121^\circ$  (571),  $119^\circ$  (566)).]

*With aromatic secondary amines.* [ $\bar{C}$  htd. with *N*-methylaniline at  $100^\circ$  (521) (525) in pres. of aq.  $Na_2CO_3$  (160), or  $\bar{C}$  with *N,N*-dimethylaniline +  $I_2$  at  $150^\circ$  (504), or  $\bar{C}$  with mixt. of *N*-methylaniline and *N,N*-dimethylaniline at  $150^\circ$  (526), gives (yields: 92.5% (526), 60% (525), 41% (521)) *N*-benzyl-*N*-methylaniline (benzyl-methyl-phenylamine) [Beil. XII-1024, XII<sub>1</sub>-(450)], b.p.  $305$ – $306^\circ$  (527),  $187$ – $188^\circ$  at 26 mm. (525),  $177$ – $178^\circ$  at 18 mm. (526),  $171^\circ$  at 13 mm. (528),  $162$ – $163^\circ$  at 8 mm. (504);  $D_{26}^{20} = 1.0421$  (504),  $D_4^{25} = 1.0475$  (528);  $n_D^{25} = 1.6006$  (504), 1.6071 (528). ( $\bar{B}$ .P.KOH, m.p.  $131^\circ$  (529),  $128$ – $128.5^\circ$  (504),  $127^\circ$  (525),  $109^\circ$  (530),  $105$ – $107^\circ$  (531),  $104^\circ$  (532),  $103.0$ – $103.5^\circ$  (533); note disagreement)]

[ $\bar{C}$  htd. with *N*-ethylaniline (534) in toluene +  $Na_2CO_3$  (535), or  $\bar{C}$  with *N,N*-diethylan-



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iline +  $I_2$  at  $150^\circ$  (504), or  $\bar{C}$  with a mixt. of *N*-ethylaniline + *N,N*-diethylaniline at  $150^\circ$  (526), gives *N*-benzyl-*N*-ethylaniline (benzyl-ethyl-phenylamine) [Beil. XII-1026, XII<sub>1</sub>- (450)], b. p.  $285-286^\circ$  sl. dec. at 710 mm. (534),  $212-220^\circ$  at 54 mm. (526),  $185.5-186.5^\circ$  at 22 mm. (535) (536),  $173^\circ$  at 12 mm. (528),  $163-164^\circ$  at 6 mm. (504);  $D_4^{15} = 1.0330$  (528);  $n_D^{25} = 1.5975$  (528) ( $\bar{B}$ .  $PhOH$ , m. p.  $116-117^\circ$  (536),  $114^\circ$  (535),  $113-114^\circ$  (504),  $111-112^\circ$  (533)). — For important study of sulfonation of *N*-benzyl-*N*-ethylaniline see (537).]

*With heterocyclic secondary amines.*  $\bar{C}$  with piperidine reacts vigorously giving (538) (541) (542) *N*-benzylpiperidine [Beil. XX-23, XX<sub>1</sub>- (8)], b. p.  $248^\circ$  (539),  $245-247^\circ$  (540),  $245^\circ$  (538) (541),  $119^\circ$  at 13 mm. (542);  $D_4^{20} = 0.96049$  (542),  $D_4^{16} = 0.9625$  (541),  $D_4^{15} = 0.96451$  (542);  $n_D^{20} = 1.52269$  (542) ( $\bar{B}$ .  $HCl$ , m. p.  $178^\circ$  (543)).]

[Direct reaction of  $\bar{C}$  with morpholine appears never to have been reported; the expected product, viz., *N*-benzylmorpholine [Beil. XXVII-7, XXVII<sub>1</sub>- (203)] (544), has, however, been prepd. by many other methods and has following constants: b. p.  $260-261^\circ$  cor. (545),  $136-136.5^\circ$  at 14 mm. (544),  $128-129^\circ$  at 13 mm. (542);  $D_4^{20} = 1.03874$ ,  $D_4^{15} = 1.03396$  (542) ( $\bar{B}$ .  $HCl$ , m. p.  $244-245^\circ$  dec. (545),  $\bar{B}$ .  $PhOH$ , m. p.  $193.5-195^\circ$  cor. (544),  $184-185^\circ$  (545)).]

*With aliphatic tertiary amines.*  $\bar{C}$  with  $(CH_3)_3N$  in abs. alc. (546) (561) (563) or abs.  $MeOH$  at  $0^\circ$  (572) gives trimethyl-benzyl-ammonium chloride [Beil. XII-1020, XII<sub>1</sub>- (448)], m. p.  $235^\circ$  (572) dec. (546); for studies of behavior of this prod. toward cat. hydrogenation see (573) (574).]

$\bar{C}$  with  $(C_2H_5)_3N$  directly (563) or at  $100^\circ$  in s.t. (567) of (570) gives triethyl-benzyl-ammonium chloride [Beil. XII-1021], but its constants are not reported.]

*With aromatic tertiary amines.*  $\bar{C}$  with *N,N*-dimethylaniline at ord. temp. (575) (577) in  $MeOH$  or  $EtOH$  (576) gives dimethyl-phenyl-benzyl-ammonium chloride [Beil. XII-1025, XII<sub>1</sub>- (450)], tble. of monohydrate from aq. or alc., m. p.  $110^\circ$  (575),  $109.5^\circ$  (578), m. p. anhydrous form,  $116^\circ$  (577); for studies of rate of formn. of this salt in  $MeOH$  at  $29^\circ$  and  $38^\circ$  see (570), for studies of behavior on cat. hydrogenation see (573) (580); for use of this quaternary salt as reagt. for introduction of benzyl radical see (473).]

$\bar{C}$  with *N,N*-diethylaniline in dry  $C_6H_6$  refluxed 30 min. gives (581) diethyl-phenyl-benzyl-ammonium chloride, m. p.  $104^\circ$  (581).]

*With heterocyclic tertiary amines.*  $\bar{C}$  with pyridine directly (582) (583) (584) (585) (586) or on htg. at  $150^\circ$  for 6 hrs. (587) gives *N*-benzylpyridinium chloride [Beil. XX-218, XX<sub>1</sub>- (74)], but this salt is difficult to crystallize (586) and its properties are not well established; for kinetics of the addition see (4) (579). — Note that  $\bar{C}$  with pyridine in pres. of  $Cu$  on htg. gives (588) a mixt. of 2-benzylpyridine and 4-benzylpyridine, but this type of nuclear benzylation cannot be discussed here.]

*With arylhydrazines.*  $\bar{C}$  (1 mole) with phenylhydrazine (2 moles) mixed with cooling (589) and subsequently htd. at  $115-120^\circ$  (590) (591) (592), or refluxed in alc. (593), or  $\bar{C}$  with phenylhydrazine +  $Na$  in  $C_6H_6$  (594) or liq.  $NH_3$  (595), or  $\bar{C}$  with phenylhydrazine +  $NaNH_2$  in liq.  $NH_3$  (73% yield (595)), gives *N*-benzyl-*N*-phenylhydrazine ( $\alpha$ -benzyl-phenylhydrazine) [Beil. XV-532, XV<sub>1</sub>- (164)], oil, b. p.  $216-218^\circ$  at 38 mm. (591),  $207-208^\circ$  at 10 mm. (593) ( $\bar{B}$ .  $HCl$ , m. p.  $176-177^\circ$  (596),  $170^\circ$  (593),  $164-169^\circ$  (595),  $167^\circ$  (594) (595),  $166-167^\circ$  (590); corresp. acetyl deriv., m. p.  $121-122^\circ$  (594) (595); corresp. benzoyl deriv., m. p.  $139-140^\circ$  (590)); note that the *N*-benzyl-*N*-phenylhydrazine is often accompanied (593) (591) by some benzaldehyde *N*-benzyl-*N*-phenylhydrazone, m. p.  $111-112^\circ$  (590),  $111^\circ$  (593) (594). — The isomeric *N*-benzyl-*N'*-phenylhydrazine ( $\beta$  or *sym*-benzyl-phenylhydrazine) [Beil. XV-533, XV<sub>1</sub>- (165)], m. p.  $35-36^\circ$ , is not obtd. by benzylation of phenylhydrazine but only by indirect methods.]

[For analogous use of  $\bar{C}$  in prepn. of *asym*-benzyl-*o*-tolylhydrazine, *asym*-benzyl-*m*-tolylhydrazine, *asym*-benzyl-*p*-tolylhydrazine, etc., see (597).]

*With arylhydroxylamines.*  $\bar{C}$  with *N*-phenylhydroxylamine in pyridine as directed

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(3557); (3558); (3559); (3560); (3561); (3562); (3563); (3564



Colorless crystals from alc. (2).

[For prepn. of  $\bar{C}$  (30-50% yield of mixed solid + liquid stereomers (2)) from 1,2-dichloroethylene (3:5030) + 1,1,2-trichloroethane (3:5330) + 1%  $AlCl_3$  for 5 days at 35-40° sec (2); for formn. of  $\bar{C}$  from 1,2-dichloroethylene (3:5030) with  $HCl$  +  $AlCl_3$  at 50° see (1).]


$\bar{C}$  in  $CCl_4$  treated with  $AlCl_3$  remains colorless and the solution does not (2) evolve  $HCl$ , even on boilg.

$\bar{C}$  in alc. treated with  $Zn$  dust gives (80% yield (2)) 1-chlorobutadiene-1,3 (3:7210), b.p. 68° (2).

$\bar{C}$  dissolved in hot alc. and titrated with  $N/10$   $KOH$  splits off 1.44-1.50 moles  $HCl$  (2).

[A pentachlorobutane obtained (3) from trichloroethylene (3:5170) + 1,1-dichloroethane (3:5035) +  $AlCl_3$  may or may not be identical with  $\bar{C}$ .]

3:0750 (1) Müller, Hönn, *J. prakt. Chem.* (2) 128, 289-290 (1932). (2) Prins, *Rec. trav. chim.* 50, 121-123 (1937). (3) Consortium für Elektrochem. Ind., *Brit.* 453,414, Oct. 8, 1930; *Cent.* 1937, 1 1012.

3:0765 *p*-CHLOROBENZALDEHYDE  $Cl$    $CHO$   $C_7H_5OCl$  *Bel.* VII - 235  
VII<sub>1</sub>-(133)

M.P. 49°	(1)	B.P. 214.5-210.5° at 760 mm.	(3)
48°	(2) (3)	213-214°	(6) (8)
47.6°	(4) (6)	213°	at 748 mm. (6)
47°	(5)	108-111°	at 25 mm. (7)
40-47°	(7)		

Colorless pl. with odor like benzaldehyde. — Volatile with steam. — Somewhat sol. cold aq., more sol. hot aq.; eas. sol. alc., ether,  $C_6H_6$ ,  $CS_2$ ,  $AcOH$ . — Forms spar. sol.  $NaHSO_3$  cpd.

[For prepn. of  $\bar{C}$  from *p*-chlorotoluene (3:8287) with  $CrO_2Cl_2$  (10), or by halogenation to *p*-chlorobenzal (di)chloride (3:0700) (7) (46) or *p*-chlorobenzal (di)bromide (11) and their subsequent hydrolysis with fuming  $H_2SO_4$  (6) (12) (13), conc.  $H_2SO_4$  (7), anhydrous oxalic acid (8), or water in a s.t. at 170° (14) (15) see indicated refs.; from *p*-aminobenzaldehyde by diazotization and reactn. with  $CuCl$  (73% yield (10)) see (10) (17) (1); from *p*-chlorobenzyl chloride (3:0220) (or bromide) by boilg. with aq.  $Pb(NO_3)_2$  in  $CO_2$  (4) (5) or with hexamethylenetetramine (2); from *p*-chlorobromobenzene via *p*-chlorophenyl  $MgBr$  and its reactn. with ethyl orthoformate (64% yield) (18); from *p*-chlorobenzonitrile with  $SnCl_2$  (10); from chlorobenzene +  $HCN$  +  $AlCl_3$  (20) or with  $CO$  +  $AlCl_3$  (21); from *p*-chlorobenzylamine with hexamethylenetetramine (45) see indic. refs.]

$\bar{C}$  with  $KMnO_4$  (2) (4) (5) or even slowly in air oxidizes to *p*-chlorobenzoic ac. (3:4910), m.p. 236°. [For study of auto-oxidation see (22).] —  $\bar{C}$  on cat. hydrogenation (92% yield (23)) or electrolytic reductn. (24) or by actn. of iodo-magnesium hydrobenzoate (84% yield (25)) gives *p*-chlorobenzyl alc., ndls. from  $C_6H_6$ /gr., m.p. 71-72.5° (23). —  $\bar{C}$  with conc. alk. undergoes Cannizzaro reactn. (for study see (20) (28)) although presumable products, *p*-chlorobenzyl alc. and *p*-chlorobenzoic ac., have not been (by this reactn.) actually isolated. [For study of  $\bar{C}$  in mixed Cannizzaro reactn. see (27).]

$\bar{C}$  on reduction with  $Ni/Al$  alloy (Raney  $Ni$ ) in aq. alk. gives (60% yield (48)) toluene (1:7405).

$\bar{C}$  with dil.  $KCN$  gives benzoin condensation yielding 4,4'-dichlorobenzoin, m.p. 85-87° (26), which on oxidn. with  $HNO_3$  in  $AcOH$  yields 4,4'-dichlorodibenzil, m.p. 165-166° (29).

$\bar{C}$  on litg. with  $NaOAc$  +  $Ac_2O$  for 8 hrs. at 180-200° undergoes Perkin reactn. giving (yield: 52% (13), 60% (17)) *p*-chlorocinnamic ac., m.p. 240-250° (17), 247° (13) (31). [This with  $Br_2$  in  $CHCl_3$  gives (30) *p*-chlorocinnamic acid dibromide, m.p. 161° (30).] —  $\bar{C}$  + malonic acid + pyridine gives alm. quant. yield (31) *p*-chlorocinnamic acid. [With-





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### 3:8538 ETHYL $\beta$ -CHLOROCROTONATE



Beil. II - 416



B.P. [184° cor.	(1)]	$D_4^{20} = 1.106$ (3)	$n_D^{20} = 1.4587$ (3)
179-180°	(2)	1.101 (7)	
77° at 15 mm.	(3)	$D_4^{19.2} = 1.1018$ (7)	$n_D^{19.6} = 1.4588$ (4)
76-77° at 14 mm.	(4) (5)		
75.3-76.0° at 14 mm.	(6)	$D_4^{17.9} = 1.1526$ (6)	$n_D^{17.9} = 1.4509$ (6)
66° at 10 mm.	(7)		

[See also ethyl  $\beta$ -chloroisocrotonate (3:8325).]

[For prepn. of  $\bar{C}$  from  $\beta$ -chlorocrotonic acid (3:2625) in EtOH with HCl gas (100% yield (2)) (4) or with conc.  $\text{H}_2\text{SO}_4$  (7) see indic. refs.]

[For formn. of  $\bar{C}$  from ethyl acetoacetate (1:1710) with  $\text{PCl}_5$  as a by-product of prepn. of ethyl  $\beta$ -chloroisocrotonate (3:8325) see (8) (9), but this is definitely not a good means of prepn. of  $\bar{C}$ .]

[ $\bar{C}$  with Al/Hg in alc. on warming is both dehalogenated and hydrolyzed yielding (10) crotonic acid (1:0425); note that with  $\bar{C}$  this reactn. goes more readily than with the isomeric ethyl  $\beta$ -chloro-isocrotonate (3:8325).]

[ $\bar{C}$  (2 moles) with  $\text{K}_2\text{S}$  ( $1\frac{1}{2}$  moles) in 5 vols. abs. EtOH refluxed 16 hrs. (11) or  $\bar{C}$  with Na enolate of ethyl thioacetoacetate (14) gives (53% yield (11)) diethyl  $\beta,\beta'$ -thiodicrotonate

$\text{S}(-\text{C}(\text{CH}_3)=\text{CH}.\text{COOC}_2\text{H}_5)_2$ , h p. 150–153° at 4 mm. (11), accompanied by some ethyl  $\beta$ -mercaptocrotonate (see below).]

[ $\bar{\text{C}}$  with alc. NaSH (12) or alc. KSH (11) (13) gives (30% yield (13)) ethyl  $\beta$ -mercaptocrotonate; note that this prod. is apparently a mixt. of the two geom. stereoisomers of ethyl  $\beta$ -mercaptocrotonate with the corresp. keto form, viz., ethyl thioacetoacetate,  $\text{CH}_3-\text{CS}-\text{CH}_2-\text{COOC}_2\text{H}_5$ ; for details see indic. refs. — Note also that, since the same prod. results by similar treatment of the isomeric ethyl  $\beta$ -chloroisocrotonate (3:8325), a mixture of the stereoisomers can be used as the starting material.]

[ $\bar{\text{C}}$  with alkali derivs. of alcohols, phenols, mercaptans, etc., splits out alkali halide yielding corresp. ethyl  $\beta$ -substituted crotonates: e.g.,  $\bar{\text{C}}$  with Na allylate gives (9) ethyl  $\beta$ -allyloxycrotonate;  $\bar{\text{C}}$  with Na cinnamylate gives (9) ethyl  $\beta$ -cinnamyloxycrotonate;  $\bar{\text{C}}$  with Na phenolate gives (15) cf. (16) ethyl  $\beta$ -phenoxyacrylate, h.p. 147–148° at 14 mm. (15);  $\bar{\text{C}}$  with Na salt of ethyl mercaptan gives (17) ethyl  $\beta$ -ethylmercaptocrotonate, h.p. 139–141° at 16 mm. (17);  $\bar{\text{C}}$  with Na salt of benzyl mercaptan gives (90% yield (17)) ethyl  $\beta$ -benzylmercaptocrotonate, cryst. from lig., m.p. 64.5° (17). Note that in the first three of the five preceding examples either  $\bar{\text{C}}$  or the isomeric ethyl  $\beta$ -chloroisocrotonate (3:8325) or their mixture gives the same result; for the last two, however, such is not the case.]

[ $\bar{\text{C}}$  with diethyl sodiomalonate gives (5) cf. (18) *trans* diethyl  $\alpha$ -carbethoxy- $\beta$ -methyl gluconate,  $(\text{C}_2\text{H}_5\text{OOC})_2\text{CH}.\text{C}(\text{CH}_3)=\text{CH}.\text{COOC}_2\text{H}_5$  [Beil. II-853], b.p. 169–170° at 13 mm.,  $D_4^{20} = 1.0937$ ,  $n_D^{20} = 1.4595$  (5); cf. behavior of stereoisomeric ethyl  $\beta$ -chloroisocrotonate (3:8325).]

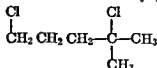
$\bar{\text{C}}$  with phenylhydrazine gives the same (2) products as obtd. from the stereoisomeric ethyl  $\beta$ -chloroisocrotonate (3:8325): e.g.,  $\bar{\text{C}}$  (1 mole) with phenylhydrazine (1 mole) at 100° for 6–8 hrs. gives by ring closure mainly (2) 3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-20, XXIV-1-(190)], pr. from aq., m.p. 127°, accompanied by small amts. of 4-benzene-azo-8-methyl-1-phenylpyrazolone-5 [Beil. XXIV-328, XXIV-1-(319)], m.p. 155–156°, and 3,3'-dimethyl-1,1'-diphenyl-bis-pyrazolone-5,5' [Beil. XXVI-484], dec. at high temp. without melting. — Note that with excess phenylhydrazine (2–4 moles) only traces of the 3-methyl-1-phenylpyrazolone-5 are formed while the amt. of the other two (less desirable) products is greatly increased (2).

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### 3:8540 *d,l*-2,5-DICHLORO-2-METHYLPENTANE

$\text{C}_6\text{H}_{12}\text{Cl}_2$

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$\text{I}_1 -$   
 $\text{I}_2 - (111)$

B.P. 179–180° (1)

[For prepn. of  $\bar{\text{C}}$  from 5-chloro-2-methylpentanol-2 [Beil. I-410, I<sub>2</sub>-(440)] with fuming HCl or AcCl sec (1); for formn. (together with other prods.) from dimethyl-cyclopropyl-carbinol [Beil. VI-10] by treatment with excess fuming HCl sec (2).]

3:8540 (1) Henry, *Compt. rend.* **143**, 1224 (1906). (2) Bruylants, Dewael, *Bull. sci. acad. roy. Belg.* (5) **14**, 148 (1923); *Cent.* 1923, I 2709; *C.A.* **22**, 3883 (1928).

3:8545 *n*-PROPYL  $\beta$ -CHLOROPROPIONATE  $C_6H_{11}O_2Cl$  Beil. II-250  
 $n-C_3H_7O.CO.CH_2.CH_2Cl$   $\Pi_1-$   
 $\Pi_2-$

B.P. 170-181° (1)

$D_4^{20} = 1.0656$  (2)

$n_D^{20} = 1.4290$  (2)

3:8545 (1) Moureu, *Ann. chim.* (7) **2**, 172 (1894). (2) Schjanberg, *Z. physik. Chem.* A-172, 231 (1935).

3:8550 *o*-CHLORO-ETHYLBENZENE



$C_8H_9Cl$

Beil. S.N. 467

B.P. 180° (1)

[For formn. of  $\tilde{C}$  from ethylbenzene (1:7410) by chlorination (other products are also formed) see (1); for formn. from chlorobenzene (3:7903) with ethylene +  $AlCl_3$  at 80° under pressure (3,5-diethyl-1-chlorobenzene is also formed) see (2).]

$\tilde{C}$  on oxidn. with alk.  $KMnO_4$  yields (1) *o*-chlorobenzoic acid (3:4150).

[ $\tilde{C}$  on hgt. with 15%  $NaOH$  +  $Cu$  powder for 2 hrs. at 315-320° in steel autoclave is thought (1) to undergo partial rearrangement, thus yielding some *m*-ethylphenol (1:1744).]

[ $\tilde{C}$  on passing through an  $Fe$  or  $Ni-Cr$  tube at 675-700° is alleged (3) to lose  $HCl$  with production of phenylethylene (styrene) (1:7435).]

[ $\tilde{C}$  on hgt. with conc.  $NH_3$  +  $CuO$  for 20 hrs. at 225° yields (2) *o*-aminoethylbenzene.]

3:8550 (1) Meharg, Allen, *J. Am. Chem. Soc.* **54**, 2920-2922 (1932). (2) Dreisbach (to Dow Chem. Co.), U.S. 2,159,370, May 23, 1939; *Cent.* 1939, II 1775; *C.A.* **33**, 6875 (1939). (3) Smith (to Naugatuck Chem. Co.), U.S. 1,687,903, Oct. 16, 1928; *Cent.* 1929, I 2922; *C.A.* **23**, 156 (1929).

3:8570 *p*-CHLORO-ETHYLBENZENE



$C_8H_9Cl$

Beil. V - 354

$V_1-(176)$

$V_2-$

B.P. 180-182°

(1)

$D_{20}^{20} = 1.0463$  (4)

180-181°

(2)

179-180°

(3) (4)

$D_4^{19} = 1.0575$  (3)

178-179° at 750 mm. (5)

$n_D^{18} = 1.5223$  (3)

75-80° at 16 mm. (5)

$n_D^{16} = 1.5235$  (4)

[For prepn. of  $\tilde{C}$  from ethylbenzene (1:7410) with  $Cl_2$  in the dark and in pres. of  $I_2$  (2) or with  $SO_2Cl_2$  +  $AlCl_3$  (1) see indic. refs.; for prepn. of  $\tilde{C}$  from chlorobenzene (3:7903) with  $EtBr$  +  $AlCl_3$  (3) or  $EtOH$  +  $AlCl_3$  (4) see indic. refs.; for prepn. of  $\tilde{C}$  from *p*-chloroacetophenone (3:6735) by reduction with  $Zn/Hg$  +  $HCl$  (27% yield) see (5).]

$\tilde{C}$  on oxidn. with  $CrO_3$  in  $AcOH$  (3) or with  $HNO_3$  (2) yields *p*-chlorobenzoic acid (3:4940), m.p. 234° (3).

[ $\tilde{C}$  on attempted nitration gives only (3) a liquid mixt. of isomers.]

[ $\tilde{C}$  with  $Br_2$  in  $AcOH$  + trace of  $I_2$  yields (2) 3-bromo-4-chloro-ethylbenzene, b.p. 143-144° at 10 mm. (2);  $\tilde{C}$  with  $Br_2$  in  $CHCl_3$  exposed in silica flask to sunlight yields (2) *p*-chloro- $\alpha$ -bromo-ethylbenzene, b.p. 120-121° at 8 mm. (2)]

[ $\bar{C}$  on htg. with 15% NaOH + Cu powder for 2 hrs. at 315-320° in a steel autoclave is thought (6) to undergo partial rearr., thus yielding *m*-ethylphenol (1:1744).]

[ $\bar{C}$  on passing through an Fe or Ni-Cr tube at 675-700° is alleged (7) to lose HCl with production of styrene (1:7435).]

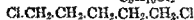
3:8570 (1) Töhl, Eberhard, *Ber.* 26, 2944 (1893). (2) Varma, Sahay, Subramonium, *J. Indian Chem. Soc.* 14, 157-159 (1937). (3) Schreiner, *J. prakt. Chem.* (2) 81, 557-558 (1910). (4) Tsukervanik, *J. Gen. Chem. (U.S.S.R.)* 8, 1512-1515 (1938); *Cent.* 1939, I 4929; *C.A.* 33, 4587 (1939). (5) Lock, Bayer, *Ber.* 72, 1068 (1939). (6) Meharg, Allen, *J. Am. Chem. Soc.* 54, 2920-2922 (1932). (7) Smith (to Naugatuck Chem. Co.), U.S. 1,687,903, Oct. 16, 1928; *Cent.* 1929, I 2922; *C.A.* 23, 156 (1929).

### 3:8575 1,5-DICHLOROPENTANE

(Pentamethylene dichloride)



Beil. 1 - 131



$I_1$ - (43)

$I_2$ - (95)

B.P.	F.P.		
182.3° cor. at 760 mm. (1)	-72.8° (1)	$D_4^{25} = 1.0940$ (3) (7)	
179.5-180.5° (2)		1.0918 (1)	
178-180° (3)			
176-178° sl. dec. (4)		$D_4^{20} = 1.1028$ (8)	$n_D^{20} = 1.4563$ (8)
102.4° at 60 mm. (8)		1.0697 (1)	
79-80° at 21 mm. (4)			
76-78° at 21 mm. (5)			
68° at 14 mm. (4)			
64-66° at 10 mm. (6)			

Colorless liq. with characteristic odor; sol. org. solv., insol. aq.

[For prepn. (yield 77-78% (1); 75-80% (4)) from *N*-benzoylpiperidine [Beil. XX-46] +  $PCl_5$  see (4) (1) (2); note that by-product benzonitrile may be removed by acid hydrolysis (4) (9) (2) or stdg. with aq. (10); for prepn. from pentanediol-1,5 (1:6519) +  $PCl_5$  in  $CCl_4$  see (5); for prepn. from *N,N*-dibenzoylpentamethylenediamine +  $SOCl_2$  see (11) (12); for formn. (19%) in direct chlorination of 1-chloropentane see (8).]

$\bar{C}$  htd. in s.t. 5 hrs. at 130° with NaCN in MeOH yields (5) 1,5-dicyanopentane (pimelonitrile) which after hydrolysis with conc. HCl at 110° for 5 hrs. (5) gives pimelic acid (1:0456), m.p. 104° (5).

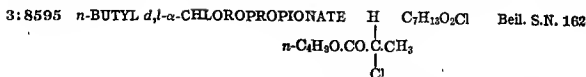
[For reaction with NaI in acetone see (8).]

⊙ 1,5-bis-(Phthalimido)pentane [Beil. XXI-493]: from  $\bar{C}$  + K phthalimide in 60-70% yield (13) by htg. at 190-200°, pale yel. ndls from  $CHCl_3$  + alc., m.p. 186° (13). [The half reaction prod., viz., 1-chloro-5-phthalimidopentane *N*-( $\epsilon$ -chloro-*n*-amyl)-phthalimide (14), has m.p. 30-31° (14).]

— Pentamethylene- $\omega, \omega'$ -bis-(isothioureahydrochloride): monohydrate, m.p. 206° (15), anhydrous epd., m.p. 210° (15). [From  $\bar{C}$  with thiourea (2 moles) in *n*-BuOH refluxed 1 hr. (15).]

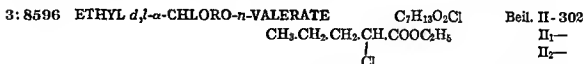
— 1,5-Diphenoxypentane (pentamethylene glycol diphenyl ether) [Beil. VI-147]: m.p. 48-49° (16); b.p. 240° sl. dec., 215-217° at 12 mm. (16). [From  $\bar{C}$  in 75% yield on protracted boilg. (30 hrs.) with large excess (3 moles) sodium phenolate in alc. (16).]

3:8575 (1) Serway, *Bull. soc. chim. Belg.* 42, 486, 488 (1933). (2) Clarke, *J. Chem. Soc.* 101, 1805 (1912). (3) Hilditch, Dunstan, *Z. Elektrochem.* 18, 883 (1912). (4) von Braun, *Ber.* 37, 2918-2920 (1904). (5) Pummerer, Schönsamgruber, *Ber.* 72, 1842 (1939). (6) East, Conn., *Oil Gas J.* 32, No. 3, 17 (1933). (7) Dunstan, Hilditch, Thole, *J. Chem. Soc.* 103, 137 (1913). (8) Hass, Huffman, *J. Am. Chem. Soc.* 63, 1233-1235 (1941). (9) von Braun, Sobocki, *Ber.* 44, 1469 (1911). (10) Zappi, *Bull. soc. chim.* (4) 19, 249 (1916).



B.P. 183.5–185.0° at 760 mm. (1)  $D_4^{20} = 1.0253$  (2)  $n_D^{20} = 1.4263$  (2)  
71.6–72.6° at 10 mm. (1)

3:8595 (1) Burkhard, Kahovec, *Monatsh.* **71**, 340 (1938). (2) Schjaneberg, *Z. physik. Chem.* A-172, 230 (1935).

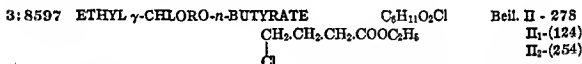


B.P. 185° at 762 mm. (1)  $D_4^{11.5} = 1.040$  (1)  $n_D^{11} = 1.43071$  (1)

Liq. with peppermint-like odor; insol. aq.; sol. alc., ether.

[For prepn. of  $\bar{C}$  from  $\alpha$ -chloro-*n*-valeronitrile with abs. EtOH + HCl see (1).]

3:8596 (1) Servais, *Rec. trav. chim.* **20**, 47–48 (1901).



B.P. 186° at 760 mm. (1)  $D_4^{20} = 1.0754$  (4)  $n_D^{20} = 1.43107$  (4)  
183–184° (2)  
77° at 16 mm. (3)  
76° at 16 mm. (4)  
72° at 16 mm. (12)  
70–71° at 10 mm. (5)  
64–66° at 10 mm. (6)

[For prepn. of  $\bar{C}$  from  $\gamma$ -chloro-*n*-butyric acid (3:0020) with EtOH +  $\text{H}_2\text{SO}_4$  (80% yield (3)) see (3); from  $\gamma$ -chloro-*n*-butyronitrile with EtOH + HCl see (2); from  $\gamma$ -ethoxy-*n*-butyric acid by htg. with  $\text{SOCl}_2$  (77% yield) see (5); from ethyl *n*-butyrate (1:3127) with  $\text{SO}_2\text{Cl}_2$  + dibenzoyl peroxide in  $\text{CCl}_4$  (40%  $\bar{C}$  + 10%  $\alpha$ - and 40%  $\beta$ -isomers) see (7); from  $\gamma$ -ethoxy-*n*-butyryl chloride (12) in almost 100% yield merely by htg. at 100° for 10 hrs. see (12).]

$\bar{C}$  added dropwise to solid KOH at 180° loses HCl and by ring closure yields (8) ethyl cyclopropanecarboxylate (Beil. IX-4, IX-1(3)), b.p. 134°.

[ $\bar{C}$  heated with NaI in acetone yields (5) (6) (9) ethyl  $\gamma$ -iodo-*n*-butyrate, b.p. 69–71° at 3 mm. (5), 84–85° at 4 mm. (9);  $\bar{C}$  with excess MeMgI yields (10) 5-chloro-2-methylpentanol-2;  $\bar{C}$  with  $\text{NaN}_3$  in aq. alc. yields (11) ethyl  $\gamma$ -azido-*n*-butyrate;  $\bar{C}$  with diethylamine in s.t. at 100° yields (3) ethyl  $\gamma$ -diethylamino-*n*-butyrate, b.p. 73–75° at 4 mm. (5).]

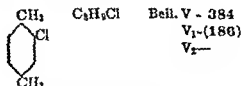
$\bar{C}$  on htg. with conc. HCl yields (5)  $\gamma$ -chloro-*n*-butyric acid (3:0020).

For the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see  $\gamma$ -chloro-*n*-butyric acid (3:0020).

Ⓒ 1-Phenylpyrrolidone-2 [Beil. XXI-237]: cryst. from aq., m.p. 69° (12). [From  $\bar{C}$  with aniline at 110° for 1 hr. (12).]

3:8597 (1) Henry, *Bull. acad. roy. Belg.* (2) 35, 507-520 (1898); *Cent.* 1898, II 273 (2) Henry, *Bull. soc. chim.* (2) 45, 341 (1886). (3) Wohlgemuth, *Ann. chim.* (9) 2, 307, 316 (1914). (4) Karvonen, *Ann. Acad. Sci. Fennicae A-10*, No. 4, p. 21; *Cent.* 1919, III 808. (5) Blicke, Wright, Zienty, *J. Am. Chem. Soc.* 63, 2489-2490 (1941). (6) Conant, Kirner, *J. Am. Chem. Soc.* 46, 249 (1924). (7) Price, Schwarcz, *J. Am. Chem. Soc.* 62, 2894-2895 (1940). (8) Rambaud, *Bull. soc. chim.* (5) 5, 1564 (1938). (9) Fuson, Arnold, Cooke, *J. Am. Chem. Soc.* 60, 2272 (1938). (10) Henry, *Compt. rend.* 143, 1223 (1906). (11) Curtius, Giulini, *Ber.* 45, 1040 (1912). (12) Prelog, Heimbach-Juhász, *Ber.* 74, 1703-1704 (1911).

3:8600 2-CHLORO-1,4-DIMETHYLBENZENE  
(*ortho*-Chloro-*p*-xylene)



B.P. 186.8°	(1)	M.P. +2°	(2)	$D_4^{15} = 1.0589$	(4)
186° at 767 mm.	(2)	+1.6°	(4)		
183.0-185.6°	(3)				
181°	(4)				
183-184°	(5)				

[For prepn. of  $\bar{\text{C}}$  from *p*-xylene (1:7415) with  $\text{Cl}_2$  in pres. of Fe (82-80% yield (4)) (5) or  $\text{I}_2$  (2), by refluxing with  $\text{PbCl}_2 \cdot 2\text{NH}_4\text{Cl}$  (6), with  $\text{SO}_2\text{Cl}_2 + \text{AlCl}_3$  (7), or with  $\text{Cl}_2$  aq. (1) see indie. refs.; for prepn. of  $\bar{\text{C}}$  from *p*-xylylene (Beil. XII-1135, XII<sub>1</sub>-(488)) via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reaction see (3).]

$\bar{\text{C}}$  on nitration with a mixt. of  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  acids as directed (4) (8) gives 5-nitro-2-chloro-1,4-dimethylbenzene, cryst. from ether, m.p. 77-78° (4), 78° (8) (accompanied by other products). [This mononitro- $\bar{\text{C}}$  on further nitration yields 5,6-dinitro-2-chloro-1,4-dimethylbenzene, cryst. from alc., m.p. 101° (4).]

$\bar{\text{C}}$  on monosulfonation with fuming  $\text{H}_2\text{SO}_4$  (2), 100%  $\text{H}_2\text{SO}_4$  (4), or chlorosulfonic acid (9) yields 2-chloro-1,4-dimethylbenzenesulfonic acid-5 (Beil. XI-127) (corresp. sulfonyl chloride, m.p. 50° (4) (9); sulfonamide, m.p. 185° (4); sulfonanilide, m.p. 155° (4)).

[ $\bar{\text{C}}$  on further chlorination yields mainly 2,5-dichloro-1,4-dimethylbenzene (Beil. V-384), m.p. 71° (2) (4), b.p. 221° cor. (2), 224° at 770 mm (4) (together with small amts. of other prods.).] [For side-chain chlorination of  $\bar{\text{C}}$  and conversion of resultant prods. by hydrolysis to 2-chlorobenzene-1-carboxylic acid-1,4 (chloroterephthalic acid) (3 4995) see (10).]

$\bar{\text{C}}$  with  $\text{Br}_2 + \text{Fe}$  (5) or with  $\text{Br}_2 + \text{HNO}_3 + \text{H}_2\text{SO}_4$  (11) as directed yields 5-bromo-2-chloro-1,4-dimethylbenzene (Beil. V-385), lts. from hot alc., m.p. 66° (5) (11). [Some dibromo- $\bar{\text{C}}$ , m.p. 93°, and tribromo- $\bar{\text{C}}$ , m.p. 234°, are also formed (5).]

3:8600 (1) Datta, Fernandes, *J. Am. Chem. Soc.* 39, 1811 (1916). (2) Kluge, *Ber.* 18, 2099 (1885). (3) Kohlrausch, Pongratz, *Monatsh.* 64, 369 (1931). (4) Wahl, *Ann. chim.* (11) 5, 5-63 (1936). (5) Wülkerodt, Wolfen, *J. prakt. Chem.* (2) 39, 402-405 (1880). (6) Seyewetz, *Biot. Compt. rend.* 135, 1121 (1902). (7) Töhl, *Ber.* 26, 2912 (1893). (8) Varma, Raman, *J. Indian Chem. Soc.* 12, 540-541 (1935). (9) E.G., *Brit.* 251,290, Jan. 25, 1928; French 611,319, Oct. 5, 1928; *Cent.* 1929, II 352. (10) I.G., French 663,791, Aug. 26, 1929; *Cent.* 1929, II 2731.

(11) Varma, Raman, *J. Indian Chem. Soc.* 12, 245 (1935).



$\bar{C}$  on oxidn. with dil.  $HNO_3$  in a s.t. yields (2) (3) 3-chloro-2-methylbenzoic acid (3:4435).

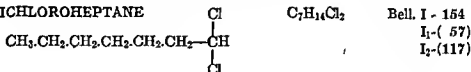
[The behavior of  $\bar{C}$  on nitration has not as yet been reported, all three possible mononitro derivatives have, however, been independently prepared; viz., 4-nitro- $\bar{C}$ , m.p.  $46^\circ$  (4); 5-nitro- $\bar{C}$ , m.p.  $101^\circ$  (5); 6-nitro- $\bar{C}$ , m.p.  $62^\circ$  (6).]

$\bar{C}$  on sulfonation yields exclusively 3-chloro-1,2-dimethylbenzenesulfonic acid-6 [Beil. XI-121] (corresp. sulfonyl chloride as yet unreported; corresp. sulfonamide, m.p.  $199^\circ$  (2)).

[ $\bar{C}$  with  $Cl_2$  in pres. of Fe yields (1) 3,4-dichloro-1,2-dimethylbenzene, b.p.  $234^\circ$ , m.p.  $8-9^\circ$  (2).]

3:8645 (1) Hinkel, Ayling, Walters, *J. Chem. Soc.* 1934, 1947-1948. (2) Krüger, *Ber.* 18, 1755-1758 (1885). (3) Claus, Bayer, *Ann.* 274, 305-311 (1893). (4) Hinkel, Ayling, Walters, *J. Chem. Soc.* 1934, 287. (5) Hinkel, *J. Chem. Soc.* 125, 1852-1853 (1924). (6) Hinkel, Collins, Ayling, *J. Chem. Soc.* 123, 2972 (1923).

### 3:8650 1,1-DICHLOROHEPTANE



B.P.  $191^\circ$  cor. (1)  
 $82-84^\circ$  at 30 mm. (2)  
 $82^\circ$  at 20 mm. (3)

$D_4^{20} = 1.011$  (3)  $n_D^{20} = 1.4440$  (3)

[For prepn. of  $\bar{C}$  from *n*-heptaldehyde (1:0183) with  $PCl_5$  at  $150^\circ$  (1) (2) (16% yield (6)), in the cold (61% yield (4)) (11), or in  $C_6H_6$  at  $20^\circ$  (3) (50% yield (5)), see indic. refs. (much loss is incurred by polymerization of the initial aldehyde by the  $HCl$  resulting in the reactn.).]

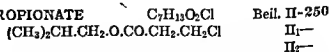
$\bar{C}$  with alc.  $KOH$  gives (1) (2) 1-chloroheptene-1 (3:8219) and on protracted actn. (1) (2) heptyne-1 (1:8085), b.p.  $100^\circ$ . —  $\bar{C}$  passed over soda-lime at  $420^\circ$  (3) (5) or htd. with powdered  $KOH$  + mineral oil at  $250^\circ$  (5) or dropped onto  $NaNH_2.C_6H_6$  (7) or treated with  $NaNH_2$  in xylene or mineral oil (60% yield (8) (10)) (9) gives *n*-amylacetylene (heptyne-1) (1:8085).

[For conversion of  $\bar{C}$  to 1,1-difluoroheptane by use of  $HgO + HF$  see (6).]

3:8650 (1) Limpricht, *Ann.* 103, 81-82 (1857). (2) Welt, *Ber.* 30, 1496 (1897). (3) Bachmann, Hill, *J. Am. Chem. Soc.* 56, 2730-2732 (1934). (4) Loevenich, Losen, Dierichs, *Ber.* 60, 951 (1927). (5) Hill, Tyson, *J. Am. Chem. Soc.* 50, 172-176 (1928). (6) Henne, Renoll, Leicester, *J. Am. Chem. Soc.* 61, 938-940 (1939). (7) Bodroux, *Compt. rend.* 208, 1023 (1939). (8) Bourgeul, *Ann. chim.* (10) 3, 223-224 (1925). (9) Meunier, Desparmet, *Bull. soc. chim.* (4) 35, 481-482 (1924). (10) Guest, *J. Am. Chem. Soc.* 47, 802 (1925).

(11) Kuz'min, *Sobshchichestvo Nauch.-Issledovatel Rabote Kiev Ind. Inst.* 2, 18 (1940); *C.A.* 37, 3047 (1943).

### 3:8655 ISOBUTYL $\beta$ -CHLOROPROPIONATE



B.P.  $191-193^\circ$  (1)

$D_4^{20} = 1.0323$  (2)  $n_D^{20} = 1.4295$  (2)

3:8655 (1) Moureu, *Ann. chim.* (7) 2, 172-173 (1894). (2) Schjaneberg, *Z. physik. Chem.* A-172, 231 (1935).

out, pyridine reactn. gives (100% yield (31)) *p*-chlorobenzal-malonic acid, m.p. 197-198° dec. (31).]

$\bar{C}$  on mononitration with conc.  $HNO_3$  + conc.  $H_2SO_4$  at 80-90° gives (32) (33) 4-chloro-3-nitrobenzaldehyde [Beil. VII-262], ndls. from  $CHCl_3$ /lgr. or from aq., m.p. 62° (32) (33); ndls. from dil. alc., m.p. 64.5° (34) [oxime, pale yel. ndls. from alc., m.p. 146° (34), 141.5-142.5° (35); phenylhydrazone, m.p. 148.5-149.5° (35), *p*-nitrophenylhydrazone, or. ndls., m.p. 278-279° (34); semicarbazone, yel. ndls., m.p. 244-245° dec. (35)].

$\bar{C}$  htd. at 100° with 1 mole aniline gives (16) (36) *p*-chlorobenzalaniline, pale yel. pl., from alc., m.p. 62° (16) (36);  $\bar{C}$  htd. with 1 mole *p*-toluidine gives (16) (36) *p*-chlorobenzal-*p*-toluidine, colorless ndls. from alc., m.p. 125° (16) (36).

[For conversion of  $\bar{C}$  with  $MeMgX$  to *p*-chlorophenyl-methyl-carbinol and dehydration of latter to *p*-chlorostyrene see (46).]

⑤ *p*-Chlorobenzaldoxime (anti form): cryst. from alc., m.p. 106-107° (6) (37). [From  $\bar{C}$  +  $NH_2OH.HCl$  +  $Na_2CO_3$  (6); the *syn* isomer has m.p. 142° (37), 140° (6), and on fusion is converted to anti isomer (6).]

⑥ *p*-Chlorobenzaldehyde phenylhydrazone: lt. yel. cryst. from dil. alc., m.p. 127-127.5° (35), 126-128° (38). [For study of kinetics of formn. see (39).]

⑦ *p*-Chlorobenzaldehyde *p*-nitrophenylhydrazone: dk. br. cryst. from alc., m.p. 216.5° u.c. (40), 224° (41), 218-220° (35).

⑧ *p*-Chlorobenzaldehyde 2,4-dinitrophenylhydrazone: or. cryst., m.p. 270° (42), 265° (45), 264° cor. (43). [Use in detn. of  $\bar{C}$  (43).]

⑨ *p*-Chlorobenzaldehyde semicarbazone: tbs. from pyridine (10), ndls. from MeOH (44, m.p. 230° (10) (47), 232-233° (44).

3:0765 (1) Blanksma, *Chem. Weekblad* 6, 909 (1909). (2) Mayer, *Englsh. Ann.* 417, 78-79 (1918). (3) Kahovec, *Kohlrausch, Z. physik. Chem.* B-38, 138 (1937). (4) Jackson, *White, Ber.* 11, 1043 (1887). (5) Jackson, *White, Am. Chem. J.* 8, 31-32 (1881). (6) Erdmann, *Schwechten, Ann.* 260, 63-65 (1890). (7) McEwen, *Org. Syntheses, Coll. Vol.* 2 (1st ed.), 133-135 (1943). (8) Erdmann, *Kirchhoff, Ann.* 247, 368 (1888). (9) Hoechst Farbwerke, *Ger.* 207,157; *Cent.* 1909, I 962. (10) Law, *Perkin, J. Chem. Soc.* 93, 1636 (1908).

(11) Lock, *Bayer, Ber.* 72, 1067 (1939). (12) Kaeswurm, *Ber.* 19, 742 (1886). (13) Böck, *Lock, Schmidt, Monatsh.* 64, 407 (1934). (14) Beilstein, *Kuhlberg, Ann.* 146, 323 (1868). (15) Beilstein, *Kuhlberg, Ann.* 147, 352-353 (1868). (16) von Walther, *Raetz, J. prakt. Chem.* (2) 65, 259-264 (1902). (17) van der Lee, *Rec. trav. chim.* 45, 678-680 (1926). (18) Bodroux, *Compt. rend.* 138, 701 (1904); *Bull. soc. chim.* (3) 31, 585-588 (1904). (19) Stephen, *J. Chem. Soc.* 127, 1874 (1925). (20) Hinkel, *Ayling, Benyon, J. Chem. Soc.* 1936, 342.

(21) *Ger.* 281,212, Dec. 15, 1914, *Cent.* 1915, I 178; *Ger.* 403,489, Sept. 29, 1924; *Cent.* 1925, I 1369; *Brit.* 334,009, Sept. 18, 1930; *Cent.* 1930, II 3850. (22) van der Beek, *Rec. trav. chim.* 51, 411-413 (1932). (23) Carothers, *Adams, J. Am. Chem. Soc.* 46, 1681-1682 (1924). (24) Law, *J. Chem. Soc.* 99, 1114-1115 (1911). (25) Shankland, *Gomberg, J. Am. Chem. Soc.* 52, 4975 (1930). (26) Eitel, *Lock, Monatsh.* 72, 392-409 (1939). (27) Bailar, Barney, Miller, *J. Am. Chem. Soc.* 58, 2110-2111 (1936). (28) Molt, *Rec. trav. chim.* 56, 233-246 (1937). (29) Gomberg, *Van Natta, J. Am. Chem. Soc.* 51, 2241 (1929). (30) Wilsaetdt, *Ber.* 64, 2693 (1931).

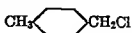
(31) K. C. Pandya, R. B. Pandya, *Proc. Indian Acad. Sci.* 14-A, 112-122 (1941); *C.A.* 36, 1599 (1942). (32) Erdmann, Ernst, *Hugbo, Ann.* 294, 380 (1897). (33) Hodgdon, *Smith, J. Soc. Chem. Ind.* 49, T408-410 (1930). (34) Hodgdon, *Beard, J. Chem. Soc.* 1927, 20. (35) van der Lee, *Rec. trav. chim.* 45, 278-281 (1926). (36) DeGaouck, *LeFevre, J. Chem. Soc.* 1938, 741-742. (37) Brady, *McHugh, J. Chem. Soc.* 125, 551 (1924). (38) Charlton, *Earl, Kenner, Luciano, J. Chem. Soc.* 1932, 40. (39) Bodforss, *Z. physik. Chem.* 109, 242 (1924). (40) Shoppee, *J. Chem. Soc.* 1931, 1232.

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 (11) Rambaud, *Bull. soc. chim.* (5) 1, 1328 (1934).

3:8660 *p*-XYLYL CHLORIDE

(*p*-Methylbenzyl chloride;  
 $\omega$ -chloro-*p*-xylene)

 $C_8H_9Cl$ 

Beil. V - 384

V<sub>1</sub>-(186)V<sub>2</sub>-(299)

B.P. 192° at 760 mm. (1)

98-101° at 27 mm. (2)

92-94° at 20 mm. (1)

90° at 20 mm. (3)

81.5° at 15 mm. (4)

 $D_4^{20} = 1.0512$  (2)  $n_D^{20} = 1.5380$  (2)

[For prepn. of  $\bar{C}$  from *p*-tolylcarbinol (1:5954) by distn. with HCl see (3) (4A) (8); by treatment with  $PCl_3$  (87% yield) see (6); for prepn. from toluene (1:7405) with paraformaldehyde + HCl (75% yield (2)) see also (5); with *sym*-dichlorodimethyl ether (3:5245) +  $ZnCl_2$  see (1) (5).]

$\bar{C}$  stood with *N*/10 alc. NaOEt at 30° yields ethyl *p*-xylyl ether [Beil. VI-493], b.p. 203°, to extent of 15% yield in 6 hrs., 40.5% in 24 hrs. (7) cf. (8) (9). [For data on rate of hydrolysis with acid or alk. in acetone soln. at 30° see (10).]

$\bar{C}$  with Mg in ether yields  $RMgCl$ ; on carbonation at 0° (11) this yields *p*- $CH_3C_6H_4CH_2COOMgCl$ ; this upon acidification presumably (no record) would yield *p*-tolylacetic ac. [Beil. IX-530], m.p. 92°; on treatment (12) with  $C_2H_5MgBr$ , however, it gives a mixt. contg. 64.2% *p*-tolylmalonic ac., sepd. with  $C_6H_6$ , cryst. from aq., m.p. 143.5-144.5° with evoln. of  $CO_2$  (12). [Use of isopropyl  $MgCl$  instead of  $C_2H_5MgBr$  gave 93% *p*-tolylmalonic ac. (12).]

$\bar{C}$  hoiled for 6 hrs. with 10 pts. 7%  $NaHCO_3$  soln. gave (66% yield (2)) *p*-tolylcarbinol (1:5054).

© *N*-(*p*-Xylyl)phthalimide [Beil. XXI-468]: from  $\bar{C}$  by htg. at 180° with K phthalimide (3); ndls. (from dil. alc.), m.p. 116-117° (3), 120° (13).

3:8660 (1) Stephen, Short, Gladding, *J. Chem. Soc.* 117, 520 (1920). (2) Shorygin, Bogdanowa, *J. Applied Chem. (U.S.S.R.)* 11, 1217-1221 (1938); *Cent.* 1939, II 1277; *C.A.* 33, 4216 (1939).

(3) *Cent. 1939, I 522*; *J. Appl. Chem.* (2) 62 111 (1900). (4) Bennett, Jones, *J. Chem. Soc.*

411. (5) Hill, Short, *J. Chem.*

(6) Franzen, *J. prakt. Chem.*

(7) von Braun, Engel, *Ann.*

(1934).

Ivanoff, Pchenitchny, *Bull. soc.*

178 (1922).

## 3:8665 4-CHLORO-1,3-DIMETHYLBENZENE

(*unsym.*-Chloro-*m*-xylene)

 $CH_3$  $C_8H_9Cl$ 

Beil. V - 373

V<sub>1</sub>-(183)V<sub>2</sub>-(291)

B.P. 192.2-193.9° (1) (?)

187-188° at 755 mm. (2)

186.5° cor. at 767 mm. (3)

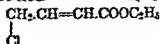
183-184° (6)

73-75° at 16 mm. (4)

 $D_{20}^{20} = 1.0598$  (3)  $n_D^{20} = 1.5230$  (5)

3:8657 ETHYL  $\gamma$ -CHLOROCROTONATE

Beil. II - 418

II<sub>1</sub>—II<sub>2</sub>-(397)

B.P. 191–193° at 760 mm. (1)

 $D_4^{15} = 1.130$  (2) $n_D^{15} = 1.4625$  (2)

84–85° at 15 mm. (2)

80° at 10 mm. (3)

77–82° at 12 mm. (4)

66–68° at 2 mm. (3)

[See also  $\gamma$ -chlorocrotonic acid (3:2170).]

Although  $\tilde{C}$  is capable of existing in two geometrically isomeric forms, only this one is known; collateral evidence (but not actual proof) indicates that  $\tilde{C}$  is the *trans* stereoisomer.

[For prepa. of  $\tilde{C}$  from ethyl vinylacetate [Beil. II-407] (5) with  $Cl_2$  in  $CCl_4$  (forming ethyl  $\beta,\gamma$ -dichloro-*n*-butyrate) followed by treatment with alc. NaOEt at 0° (splitting out HCl) and giving 65% yield see (5); from ethyl  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-butyrate [Beil. III-310, III<sub>1</sub>-(116)] by dehydration with  $P_2O_5$  (yields: 65% (4), 62.5% (3), 60% (2)) (6) (accompanied by some  $\gamma$ -chlorocrotonic acid (3:2170) (3) (2) and also by ethyl  $\gamma$ -chloro-vinylacetate (3)) see indic. refs.]

$\tilde{C}$  on hydrolysis with  $Ba(OH)_2$  below 0° or even (but less advantageously) with KOH gives (60% yield (3) (5)) (7) (2)  $\gamma$ -chlorocrotonic acid (3:2170), m.p. 83°; note, however, that hydrolysis with hot conc. alk. gives also two other products, viz.,  $O(CH_2-CH=CH-COOH)_2$ , m.p. 195° (2), and  $\gamma$ -hydroxycrotonic acid, m.p. 108° (2).

[ $\tilde{C}$  in EtOH/NaOEt undergoes addition of EtOH to unsatd. linkage followed to small extent by elimination of HCl with consequent ring closure to a cyclopropane deriv.; e.g.,  $\tilde{C}$  (0.134 mole) in 2½ pts. EtOH treated dropwise in cold with soln. of Na (0.057 mole) in the same vol. of EtOH as above gives (yields 42% (8), 25% (9)) ethyl  $\gamma$ -chloro- $\beta$ -ethoxy-*n*-butyrate, b.p. 108.0–108.5° at 20 mm.,  $D_4^{17.5} = 1.078$ ,  $n_D^{17.5} = 1.4295$  (8), accompanied by a little (3% yield (8)) ethyl 2-ethoxycyclopropane-1-carboxylate (1-carbethoxy-2-ethoxycyclopropane), b.p. 77.50–77.75° at 13 mm.,  $D_4^{13} = 0.995$ ,  $n_D^{13} = 1.453$  (8); the latter is also obt'd. (22% yield (9)) by distn. of the ethyl  $\gamma$ -chloro- $\beta$ -ethoxy-*n*-butyrate with dry powdered KOH at 180° and 45 mm. press.]

[ $\tilde{C}$  on dropwise addition to dry powdered KOH at 180° gives ethyl cyclopropane-1-carboxylate [Beil. IX-4, IX<sub>1</sub>-(3)], b.p. 130° at 728 mm.,  $D = 0.970$ ,  $n_D^{15} = 1.416$ .]

[ $\tilde{C}$  with excess dry powdered  $CaBr_2$  heated several days under reflux gives (2) (10) ethyl  $\gamma$ -bromocrotonate. —  $\tilde{C}$  (1 mole) with NaI (1 mmole) in acetone reacts readily at ord. temp. pptg. NaCl (80% theory) and yielding (3) ethyl  $\gamma$ -iodocrotonate, b.p. 92–93° at 2 mm.]

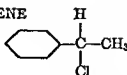
[ $\tilde{C}$  with NaOAc in AcOH heated at 100° cf. (11) yields (8) ethyl  $\gamma$ -acetoxycrotonate, b.p. 115–116° at 15 mm.,  $D_4^{23} = 1.075$ ,  $n_D^{23} = 1.4445$  (11).]

[ $\tilde{C}$  with conc. aq.  $NH_4OH$  not only has its halogen replaced by  $-NH_2$  but also is hydrolyzed with consequent formn. of  $\gamma$ -amiacrotonic acid; this was not isolatable as such but only as its picrate, the m.p. of which, however, is not reported (2).]

[ $\tilde{C}$  with  $Me_3N$  (excess) in alc. coatg. a trace of NaI in s.t. at 100° followed by evapa. with HCl gives (4)  $\gamma$ -dimethylamiacrotonic acid chloromethylate ( $\gamma$ -dimethylaminocrotonbetain chloride), m.p. 203–205° dec. (4).]

- 3:8657 (1) Lespieau, *Bull. soc. chim.* (3) 33, 466–467 (1905). (2) Rambaud, *Bull. soc. chim.* (5) 3, 139–141 (1936). (3) Braun, *J. Am. Chem. Soc.* 52, 3167–3176 (1930). (4) Linneweh, *Z. physiol. Chem.* 176, 217–221 (1928). (5) Glatfeld, Riets, *J. Am. Chem. Soc.* 67, 976 (1940). (6) Lespieau, *Compt. rend.* 130, 1410 (1900). (7) Bacher, Benninga, *Rec. trav. chim.* 55, 610 (1936).

3: 8667 *d,l*- $\alpha$ -CHLOROETHYLBENZENE  
(Methyl-phenyl-carhinyl  
chloride)

 $C_8H_9Cl$ 

Beil. V - 354  
V<sub>1</sub>-(177)  
V<sub>2</sub>-(277)

B.P. 195° dec. (1)  
194° dec. (2)  
90-91° at 33 mm. (3)  
82-83° at 18 mm. (4)  
81-82° at 17 mm. (5)  
91-92° at 16 mm. (6)  
69-70° at 13 mm. (7)  
67.5° at 12 mm. (8)  
68° at 9 mm. (9)

 $D_4^{20} = 1.0620$  (9)  $n_D^{20} = 1.5276$  (9) $D_4^{15} = 1.0598$  (6)  $n_D^{15} = 1.5337$  (6)

$\bar{C}$  even on stdg. tends to lose HCl with formn. of styrene and styrene polymers (9); such decompn. is facilitated by pres. of any HCl and  $\bar{C}$  could not be dried with  $P_2O_5$  (10).

[Both opt. act. stereoisomerides of  $\bar{C}$  are known but cannot be discussed here.]

[For prepn. of  $\bar{C}$  from methyl-phenyl-carhinol (1:6475) with 6 *N* HCl (75% yield (3)) (7), with aq. HCl in pres. of  $CaCl_2$  (2) (8), with HCl +  $ZnCl_2$  (71% yield (11)), with  $SOCl_2$  (82-88% yield (11)) (4) (5) (10), or with acetyl chloride (3:7065) (12) see indic. refs.; from ethylbenzene (1:7410) with  $Cl_2$  in light (1) (13) (14) (15) or in pres. of 1%  $PCl_5$  (90% yield (16)) see indic. refs.; from styrene (1:7435) by addn. of HCl (9) (17) (18) under press. in solvent (100% yield (19)) or at  $-80^\circ$  (68% yield (29)) see indic. refs.; for forma. of  $\bar{C}$  from methyl-phenyl-carhinyl  $MgBr$  during reaction with cyanogen chloride (47%  $\bar{C}$  + 10% methyl-phenyl-carhinyl cyanide + 5% 2,3-diphenylbutane) see (6); for formn. of  $\bar{C}$  from methyl phenyl ketone (acetophenone) (1:5515) during reduction with  $Zn/Hg$  + HCl see (20).]

[ $\bar{C}$  passed at elevated temp. over dehydrohalogenating cat. (21), or htd. with pyridine in a.t. 6 hrs. at  $130^\circ$  (77% yield (22)), or hoiled with a small excess quinoline for  $\frac{1}{2}$  hr. (75-80% yield (16)) (23), or its quat. salt with pyridine htd. in vac. (24), or htd. with acids less volatile than HCl (25), or htd. with salts of org. bases (26) (23) yields styrene (1:7435), h.p.  $145^\circ$ .]

[ $\bar{C}$  with  $H_2$  and Pd in pres. of  $MgO$  as specified (8) gives rapidly and quant. ethylbenzene (1:7410); note that  $\bar{C}$  reduces much more readily than the isomeric  $\beta$ -chloroethylbenzene (3:8712) (8).]

$\bar{C}$  on hydrolysis, e.g., by hoilg. with 25% excess of 10-15% aq.  $Na_2CO_3$  soln., gives (90% yield (16)) (27) methyl-phenyl-carbinol (1:6475) q.v.;  $\bar{C}$  with aq. alc. or with aq. alc. NaOH gives at  $50^\circ$  only (5) methyl-phenyl-carbinol; nt  $100^\circ$  both styrene (1:7435) and  $\alpha,\alpha$ -diphenyl-diethyl ether are also formed (5); under certain circumstances  $\alpha$ -diphenyl-diethyl ether may also appear (5) (1). [For study of hydrolysis of  $\bar{C}$  in acetone contg.  $HgCl_2$  see (4).]

[ $\bar{C}$  with aq.  $Na_2SO_3$  on hoilg. for 9 hrs. (14) (7) gives (43-45% yield (14)) sodium  $\alpha$ -phenylethanesulfonate (corresp. sulfinyl chloride, ndla. from alc., m.p.  $79^\circ$  (14) cf. (7), corresp. sulfonamide and anilide are unreported).]

$\bar{C}$  on oxidn. with  $Cu(NO_3)_2$  (13) nt on boilg. with aq. or dil. alc. soln. of hexamethylene-tetramine (28) gives (60% yield (13)) methyl phenyl ketone (acetophenone) (1:5515).

3:8667 (1) Schramm, *Monatsh.* 8, 101-105 (1887). (2) Engler, Bethge, *Ber.* 7, 1127 (1874). (3) Norris, Watt, Thomas, *J. Am. Chem. Soc.* 33, 1078 (1916). (4) Read, Taylor, *J. Chem. Soc.* 1940, 681. (5) Ward, *J. Chem. Soc.* 1927, 445-453. (6) Grignard, Ono, *Bull. soc. chim.* (4)



$\bar{C}$  on sulfonation (4) (5) yields exclusively 4-chloro-1,2-dimethylbenzenesulfonic acid-5 [Beil. XI-121] (corresp. sulfonyl chloride, as yet unreported; sulfonamide, ndls. from alc, m.p. 207° (4)).

$\bar{C}$  with  $Cl_2$  in pres. of Fe yields (2) 4,5-dichloro-1,2-dimethylbenzene, m.p. 76°, b.p. 240° (2).

3:8675 (1) Claus, Groneweg, *J. prakt. Chem.* (2) 43, 257 (1891). (2) Hinkel, Ayling, Walters, *J. Chem. Soc.* 1934, 1947-1948. (3) Kohlrausch, Pongratz, *Monatsh.* 64, 371 (1934). (4) Krüger, *Ber.* 18, 1756-1758 (1885). (5) Claus, Bayer, *Ann.* 274, 305-309 (1893). (6) Huntress, Seikel, *J. Am. Chem. Soc.* 61, 820 (1939). (7) Hinkel, Ayling, Walters, *J. Chem. Soc.* 1934, 286-287.

3:8680 *n*-OCTANOYL CHLORIDE  $CH_3(CH_2)_6C(=O)Cl$   $C_8H_{15}OCl$  Beil. II - 348  
(*n*-Capryloyl chloride)  $\begin{array}{c} | \\ Cl \end{array}$   $\Pi_1-$   
 $\Pi_2$ -(303)

B.P.

F.P.

195.55° at 760 mm. (1) -61.1° (1) cf. (19)  $D_4^{25} = 0.94483$  (1)

194-195° at 756 mm. (2) -63° to -62.5° cor. (19)

188-192° (3)  $D_4^{20} = 0.94866$  (1)

91° at 22 mm. (4)

83° at 16 mm. (5) (19)  $D_4^{15} = 0.95349$  (1)

74-77° at 11 mm. (6)

[104-105° at 9 mm. (18)]

 $n_D^{15} = 1.43408$  (1)

Care must be taken not to confuse  $\bar{C}$ , the acid chloride of *n*-caprylic acid, with the corresponding relatives of *n*-caproic acid ( $C_6$ ) and of *n*-capric acid ( $C_{10}$ ); for this reason the name *n*-octanoyl chloride is preferred.

[For prepn. of  $\bar{C}$  from *n*-octanoic acid (*n*-caprylic acid) (1:1145) with  $PCl_5$  (yield: 82% (19), 64% (7)), with  $PCl_3$  (2) (8), with  $PCl_3 + ZnCl_2$  (90% yield (7)), with  $SOCl_2$  (3) (96% yield (6)), or with oxalyl (di)chloride (3:5060) (18) see indic. refs.]

[For use of  $\bar{C}$  in prepn. of corresp. cellulose esters see (9) (10); for use in syntheses of glycerides see (11) (12); for use with  $AlCl_3$  in Friedel-Crafts synthesis of various ketones see (13) (14) (19); for use in prepn. of derivatives of vanillylamine see (4) (16); for cat. hydrogenation to octanaldehyde (1:0192) see (15).]

[ $\bar{C}$  with  $AlCl_3 +$  phenol yields (17) 45% *o*-(*n*-octanoyl)phenol, m.p. 22.3°, h.p. 169-170° at 11 mm.,  $D_4^{25} = 0.9989$ ,  $n_D^{25} = 1.5169$  (17) (semicarbazone, m.p. 157-158° (17)), and 38% *p*-(*n*-octanoyl)phenol, m.p. 62°, b.p. 224-225° at 10 mm. (17) (benzoate, m.p. 107-108° (17)).]

$\bar{C}$  on hydrolysis yields *n*-octanoic acid (*n*-caprylic acid) (1:1145) q.v. (for the amide, anilide, *p*-toluidide, and other derivs. corresponding to  $\bar{C}$  see 1:1145).

3:8680 (1) Deffet, *Bull. soc. chim. Belg.* 40, 389-394 (1931). (2) Henry, *Bull. acad. roy. Belg.* 1929, 252-253 (1929). (3) Hardan, *Bull.* 1929, 252-253 (1929). (4) Krafft, 89 (1939). 148 (1898). 929; *Cent.*

1929, II 2743.

(11) Heiduschka, Schuster, *J. prakt. Chem.* (2) 120, 155-156 (1928). (12) Robinson, Roche, King, *J. Am. Chem. Soc.* 54, 705-710 (1932). (13) Hartung, Munch, Deckert, Crossley, *J. Am. Chem. Soc.* 52, 3320 (1930). (14) Ralston, Bauer, *J. Org. Chem.* 5, 165-170 (1940). (15) Es-courrou, *Bull. soc. chim.* (5) 6, 1181 (1939). (16) Nelson, *J. Am. Chem. Soc.* 41, 2124 (1919). (17) Sandulesco, Girard, *Bull. soc. chim.* (4) 47, 1309-1310 (1930). (18) Averill, Roche, King, *J. Am. Chem. Soc.* 51, 868 (1929). (19) Paquette, Lingafelter, Tartar, *J. Am. Chem. Soc.* 65, 686 (1943).







3:8700 *m*-XYLYL CHLORIDE  
(*m*-Methylbenzyl  
chloride,  $\omega$ -chloro-  
*m*-xylene)

 $C_8H_9Cl$ 

Beil. V - 373  
V<sub>1</sub>-(183)  
V<sub>2</sub>-(201)

B.P. 195-196° u.c. (2)  
85-88° at 16 mm. (6)

 $D_{20}^{20} = 1.064$  (2)  $n_D^{25} = 1.5327$  (1)

[For special study of prepn. (76% yield) by chlorination of *m*-xylene (1:7420) in light see (1).]

$\bar{C}$  stood with *N*/10 alc. NaOEt at 30° yields ethyl *m*-xylyl ether [Beil. VI-494], b.p. 202°, to extent of 10.9% in 6 hrs., 32.4% in 24 hrs. (3) cf. (4). [For data on rate of hydrolysis with acid or alkali in acetone soln. at 30° see (5) ]

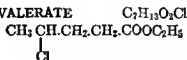
$\bar{C}$  with Mg in ether yields R.MgCl; on carbonation at 0° (7) this yields *m*-CH<sub>3</sub>.C<sub>6</sub>H<sub>4</sub>.CH<sub>2</sub>-COOMgCl; this upon acidification presumably (no record) would yield *m*-tolylacetic acid [Beil. IX-528], m.p. 61°; upon treatment (8) with C<sub>2</sub>H<sub>5</sub>MgBr, however, it gives a mixt. contg. 57.6% *m*-tolylmalonic acid, colorless pdr. from CHCl<sub>3</sub>, m.p. 130-131° with loss of CO<sub>2</sub> (8). [Use of isopropyl MgCl in place of C<sub>2</sub>H<sub>5</sub>MgBr gave 88% of *m*-tolylmalonic ac. (8).]

$\bar{C}$  on boiling with Pb(NO<sub>3</sub>)<sub>2</sub> soln. (2), or Cu(NO<sub>3</sub>)<sub>2</sub> soln. (30% yield (6)), or alk. Na<sub>2</sub>CrO<sub>4</sub> (90% yield (6)) gives *m*-tolualdehyde (1:0208).

Ⓢ *N*-(*o*-Xylyl)phthalimide [Beil. XXI-467]: adls. from alc., m.p. 117-118°. [Reported (9) from *m*-xylyl bromide and therefore presumably obtainable under appropriate conditions from  $\bar{C}$ .]

3:8700 (1) King, Merriam, *Proc. Nova Scotian Inst. Sci.* 18, 276-281 (1933/34); *C.A.* 29, 6214 (1935); *Cent.* 1935, II 2359. (2) Gundelach, *Bull. soc. chim.* (2) 26, 43 (1876). (3) Franzen, *J. prakt. Chem.* (2) 97, 83-84 (1918). (4) Olivier, *Rec. trav. chim.* 41, 306-307 (1921). (5) Olivier, Weber, *Rec. trav. chim.* 53, 885 (1934). (6) Posner, Schreiber, *Ber.* 57, 1131, 1137 (1924). (7) Ivanoff, Spassoff, *Bull. soc. chim.* (4) 9, 20 (1931). (8) Ivanoff, Fehenatchny, *Bull. soc. chim.* (5) 1, 227 (1934). (9) Brömme, *Ber.* 21, 2700 (1888).

3:8703 ETHYL *d,l*- $\gamma$ -CHLORO-*n*-VALERATE

 $C_7H_{13}O_2Cl$ 

Beil. II - 302

II<sub>1</sub>-(131)II<sub>2</sub>—

B.P. 196° (1)  
70.5° at 9 mm. (2)

 $D_4^{20} = 1.0393$  (1)  $n_D^{20} = 1.4310$  (1)

Oil with odor like amyl acetate.

[For prepn. of  $\bar{C}$  from  $\gamma$ -chloro-*n*-valeric acid (3:9270) + EtOH + H<sub>2</sub>SO<sub>4</sub> see (1); from  $\gamma$ -n-valerolactone (1:5080) with HCl in EtOH see (3).] [For the opt. active isomers of  $\bar{C}$  see Beil. II<sub>2</sub>-(268) and subsequent literature ]

3:8703 (1) Schjanberg, *Ber.* 70, 2385-2391 (1937). (2) Wohlgermuth, *Compt. rend.* 158, 1578 (1914); *Ann. chim.* (9) 2, 300-301 (1914). (3) Noyes, Cox, *J. Am. Chem. Soc.* 25, 1094 (1903).



Lachrymatory oil.

[For prepn. (88% yield) from *o*-tolylcarbinol (1:5922) by action of thionyl chloride and pyridine see (2), by action of  $H_2SO_4 + HCl$  (85-92% yield) see (3); the prepn. from *o*-xylene (1:7430) by action of trioxymethylene +  $HCl$  gives a mixture of  $\bar{C}$  and *p*-xylyl chloride (3:8660) (4) (5) (6).]

$\bar{C}$  stood with  $N/10$  alc. NaOEt at  $30^\circ$  yields ethyl *o*-xylyl ether [Beil. VI-484], oil, b.p.  $208-210^\circ$ , to extent of 21% in 6 hrs., 52% in 24 hrs. (7) cf. (8). [For data on rate of hydrolysis with acid or alkali in acetone soln. at  $30^\circ$  see (9).]

$\bar{C}$  with Mg in ether yields  $R.MgCl$ ; no carbonation at  $0^\circ$  (10) thus yields  $o-CH_3.C_6H_4.CH_2.COOMgCl$ ; this upon acidification presumably (no record) would yield *o*-tolylacetic acid [Beil. IX-527], m.p.  $88-89^\circ$ ; upon treatment (11) with  $C_2H_5MgBr$ , however, it gives 83.3% yield of *o*-tolymalonic ac., ndls. from aq., m.p.  $139-140^\circ$ , with loss of  $CO_2$  (11), + 16% yield of *o*-tolylacetic ac.

$\bar{C}$  refluxed 5 hrs. with dil. alc. KCN gives 74% yield (2) *o*-tolylacetonitrile [Beil. IX-527], b.p.  $244^\circ$ , which on boiling 1 hr. with dil.  $H_2SO_4$  (2) gives 73% yield (2) of *o*-tolylacetic ac. [Beil. IX-527], ndls. from aq., m.p.  $88-89^\circ$ .

$\bar{C}$  on warming at  $100^\circ$  with 1.3 moles pyridine gives ppt. of *o*-xylylpyridinium chloride, cryst. from  $CH_3OH +$  dry ether, m.p.  $183^\circ$  (12).

⑥ *N*-(*o*-Xylyl)phthalimide [Beil. XXI-467]: cryst. from alc., m.p.  $148-149^\circ$ . [Reported (13) from *o*-xylyl bromide and therefore presumably obtainable under appropriate conditions from  $\bar{C}$ .]

3:8710 (1) Reyman, *Bull. soc. chim.* (2) 26, 534 (1876). (2) Hill, Short, *J. Chem. Soc.* 1935, 1125. (3) Reichstein, Cohen, Ruth, Meldahl, *Helv. Chim. Acta* 19, 415 (1936). (4) Darzens, *Compt. rend.* 208, 818-820 (1939). (5) Shorygin, Skoblinakaya, *J. Gen. Chem. (U.S.S.R.)* 6, 31, 2196 (1937). (6) Hoch, *Compt. rend.* 192, 1465 97, 83 (1915). (8) Olivier, *Rec. trav. chim.* 41, 306 n. 53, 885 (1934). (10) Ivanoff, Spassoff, *Bull. soc. chim.* (4) 9, 20 (1931).

(11) Ivanoff, Fehenitchny, *Bull. soc. chim.* (5) 1, 226 (1934). (12) von Braun, Nelles, *Ber.* 70, 1762 (1937). (13) Strassmann, *Ber.* 21, 576 (1888).

### 3:8712 $\beta$ -CHLOROETHYLBENZENE

( $\omega$ -Chloroethylbenzene,  
 $\beta$ -phenylethyl chloride,  
benzylcarbinyl chloride)



$C_8H_9Cl$

Beil. V<sup>-</sup>-(354)

V<sub>1</sub>-(177)

V<sub>2</sub>-(277)

B.P.

197-198°

(1)

B.P. (cond.)

88°

at 16 mm. (9)

$D_4^{25} = 1.069$  (14)

192-198° dec. at 760 mm. (2)

82-84°

at 16 mm. (2)

190-200° sl. dec. (3)

83-84°

at 14 mm. (10)

$n_D^{20} = 1.5294$  (11)

96° at 23 mm. (4)

81-84°

at 14 mm. (11)

91-92° at 20 mm. (3) (5)

85-86°

at 12 mm. (5)

80° at 20 mm. (6)

79°

at 12 mm. (12)

94-96° at 18 mm. (7)

68.5-69°

at 4 mm. (13)

89-92° at 16 mm. (8)

Colorless oily liquid.

[For prepn. of  $\bar{C}$  from  $\beta$ -phenylethyl alc. (1:6505) with fuming  $HCl$  in s.t. 4 hrs. at  $140^\circ$  (57% yield (13)) (15), with conc.  $HCl + ZnCl_2$  (82% yield (8)), with 6*N*  $HCl$  (small yield (16)), with  $PCl_5$  in  $CHCl_3$  (yield 70% (3)) (10) (12) (prod. conts P compounds (10) removed with  $NaHCO_3$  (12)) or in  $CCl_4$  (50% yield (5)), with  $SOCl_2$  at room temp. (yields:

**3:0780 4-CHLORO-2-METHYLPHENOL**  
 (4-Chloro-o-cresol)
 $C_7H_7OCl$ 
 Beil. VI - 350  
 VI<sub>1</sub>-(174)  
 VI<sub>2</sub>-(332)

 M.P. 48-49° (1) (5) B.P. 220-225° (1) (2) (5)  
 45° (2)

Nds. (from pet. eth.).

[For prepn. from o-cresol (1:1400) by chlorination with  $SO_2Cl_2$  see (1) (5).]

$\bar{C}$  dislvd. in 5 pts. AcOH and treated with small excess of conc.  $HNO_3$  ( $D = 1.42$ ) yields (3) 6-nitro-4-chloro-2-methylphenol [Beil. VI<sub>1</sub>-(178)], yel. ndls., m.p. 107° (3), eas. sol. alc.,  $C_6H_6$ , less sol. AcOH, acetate, m.p. 88° (3).

$\bar{C}$  htd. with phthalic anhydride (1:0725) +  $NaCl \cdot AlCl_3$  at 150-200° for 2 hrs. yields (4) after decompn. with  $HCl$ , and repeated recrystn. from  $C_6H_6$ , AcOH, xylene, 1-hydroxy-2-methyl-4-chloroanthraquinone, yel.-br. cryst., m.p. 177-179° (4).

$\bar{C}$  htd. with  $KOH + CH_3I$  yields (1) 4-chloro-2-methylanisole, volatile with steam, b.p. 212.6-214.6° cor. at 758 mm. (1).

④ 4-Chloro-2-methylphenyl benzoate: from  $\bar{C} + BzCl + aq. NaOH$ ; lfts. from pet. eth., m.p. 71-72° (1).

3:0780 (1) Perntoner, Condorelli, *Gazz. chim. ital.* 28, I 211 (1898). (2) Klarmann, Shternov Gates, *J. Am. Chem. Soc.* 55, 2585 (1933). (3) Zincke, *Ann.* 417, 222-223 (1918). (4) Waldmann, Sellner, *J. prakt. Chem.* 150, 152 (1938). (5) Sah, Anderson, *J. Am. Chem. Soc.* 63, 3105 (1941).

**3:0810 1,6-DICHLORONAPHTHALENE**  
 (2,5-Dichloronaphthalene)
 $C_{10}H_6Cl_2$ 
 Beil. V - 543  
 V<sub>1</sub>-(202)  
 V<sub>2</sub>-(446)

 M.P. 49° (1) (2)  
 48.5-49° (3)  
 48° (4) (5) (9) (12) (13) (18) (10)  
 47-48° (11)

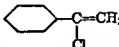
Nds. from alc. — Volatile with steam. — Sublimes.

[For prepn. of  $\bar{C}$  from naphthalenedisulfonic acid-1,6 [Beil. XI-213] (16), from K salt of 6-chloronaphthalenesulfonic acid-1 [Beil. XI-161] (4), from 6-chloronaphthalenesulfonyl chloride-1 [Beil. XI-161] (7), from 6-bromonaphthalenesulfonyl chloride-1 [Beil. XI-165] (8), from 5-chloronaphthalenesulfonyl chloride-2 [Beil. XI-180] (7), from 5-nitronaphthalenesulfonyl chloride-2 [Beil. XI-186] (9), from 6-chloronaphthol-1 (3:2615) (5), or from naphthalene-1,6-bis-(sulfonyl chloride) [Beil. XI-214] (10) (3) (6) by htg. with  $PCl_5$  as directed see indic. refs.; for prepn. of  $\bar{C}$  from 5-chloronaphthalenesulfonyl chloride-1 or 6-chloronaphthalenesulfonyl chloride-1 (both above) by htg. at 210-250° see (7); for prepn. of  $\bar{C}$  from 6-chloronaphthylamine-2 via diazotization and use of  $Cu_2Cl_2$  reactn. see (2); from 6-sulfonaphthylamine-1 [Beil. XIV-758, XIV<sub>1</sub>-(735)] or from 5-sulfonaphthylamine-2 [Beil. XIV-748, XIV<sub>1</sub>-(733)] via treatment of corres. diazonium salt with  $PCl_5$  in  $PCl_5$  see (11); from 1,6-diaminonaphthalene [Beil. XIII-204] by tetrazotization in  $HCl$  and htg. with  $Cu$  pdr. (24% yield (3)) (12) (13) see indic. refs.; for prepn. of  $\bar{C}$  from 1,6-dichloronaphthalenedisulfonic acid-4,8 [Beil. XI-213] or from 1,6-dichloronaphthalenedisulfonic acid-3,8 [Beil. XI-214] via hydrolysis of the  $-SO_3H$  group by htg. with dil.  $H_2SO_4$  in a.t.

(11) Whitmore, Thorpe, *J. Am. Chem. Soc.* **55**, 785 (1933). (12) Paal, Müller-Lobeck, *Ber.* **64**, 2148-2150 (1931). (13) Conant, Kirner, *J. Am. Chem. Soc.* **46**, 241, 249 (1924). (14) Dunstan, Hilditch, Thole, *J. Chem. Soc.* **103**, 140 (1913). (15) von Braun, Deutsch, *Ber.* **45**, 1268-1269 (1912). (16) Norris, Watt, Thomas, *J. Am. Chem. Soc.* **38**, 1078 (1916). (17) Darzens, *Compt. rend.* **152**, 1316 (1911). (18) Carré, Libermann, *Compt. rend.* **198**, 274-276 (1934). (19) Gilman-Beaber, *J. Am. Chem. Soc.* **45**, 842 (1923). (20) Ashworth, Burkhardt, *J. Chem. Soc.* **1928**, 1798-1799.

(21) Suter, Evans, *J. Am. Chem. Soc.* **60**, 537 (1938). (22) Madinaveitia, *Bull. soc. chim.* (4) **25**, 604 (1924). (23) Shoenberger, *J. Chem. Soc.* **1927**, 104-105. (24) Shoemsmith, Connor, *J. Chem. Soc.* **1927**, 1-247 (1870). (25) Schramm, *Monatsh.* **8**, 1-247 (1870). (26) Schramm, *Monatsh.* **8**, 1-247 (1870). (27) Scher, Schmitz, *Ber.* **39**, 2209-2210 (1906). (28) Cou, *J. Gen. Chem.* **1**, 1-247 (1870). (29) Shorugin, Losev, *J. Gen. Chem.* **1**, 1-247 (1870). (30) Kindler, *Ann.* **452**, 119-120 (1927).

*Chem.* **8**, 199-200 (1943).

**3:8715**  $\alpha$ -CHLOROVINYLBENZENE   $C_8H_7Cl$  **Beil. V - 476**  
( $\alpha$ -Chlorostyrene)  $V_1$ -(230)  
 $V_2$ -(367)

B.P.		F.P.	
109°	(1)	-24° to -23° (5)	$D_4^{24.6} = 1.0983$ (2)
83.5-84° at 23 mm.	(2)		$n_D^{24.6} = 1.55898$ (2)
85.0-85.5° at 22.5 mm.	(3)		$D_4^{20} = 1.101$ (2)
80-83° at 21 mm.	(13)		1.0975 (3)
73° at 16 mm.	(4)		1.0916 (3)
73-74° at 16 mm.	(3)		$n_D^{20.5} = 1.5584$ (5)
61° at 9 mm.	(5)		$D_4^{13} = 1.12$ (4)
			$n_D^{20} = 1.5600$ (13)
			$n_D^{15} = 1.5645$ (4)
			$n_D^{17} = 1.56199$ (2)
			$D_4^{17} = 1.1030$ (2)
			$D_4^{18.6} = 1.1024$ (2)
			$n_D^{18.5} = 1.56226$ (2)

Colorless liq. with arom. odor soon changing to that of formaldehyde and benzoyl chloride from air oxidation (5). —  $\bar{C}$  could not be polymerized even in u.v. light, by peroxides or  $SnCl_4$  (12).

[For prepn. of  $\bar{C}$  from methyl phenyl ketone (acetophenone) (1:5515) with  $PCl_5$  see (2) (1) (5) (6), from  $\alpha,\alpha$ -dichloroethylbenzene ("acetophenone dichloride") on htg. see (7); from  $\beta$ -bromo- $\alpha$ -chloroethylbenzene (styrene chloro-bromide) with alc. KOH in the cold (70% yield) see (4); from  $\alpha,\beta$ -dichloroethylbenzene (styrene dichloride) (3:6685) with aq. alc. NaOH at 50-60° (89% yield) see (13)]

$\bar{C}$  on boudg. with conc.  $HCl$  (4) (1), or  $\bar{C}$  with 80%  $H_2SO_4$  at 50° for 4 hrs. (13) cf. (14), gives (81% yield (13)) cf. (14) acetophenone (1:5515).

$\bar{C}$  is resistant to actn. of alc. KOH (5);  $\bar{C}$  on refluxing for 13 hrs. with very conc. alc. NaOEt gives (8) some phenylacetylene (1:7425) together with other prods. (5).

[ $\bar{C}$  with NOCl yields (9)  $\alpha,\beta$ -trichlorostyrene, b.p. 148–150° at 20 mm. (9);  $\bar{C}$  htd. with alc. KCN in s.t. at 200–220° yields (10) phenylsuccinonitrile which on saponification gives phenylsuccinic acid (1:0790);  $\bar{C}$  with Na in liq.  $NH_3$  gives (15% yield (10)) ethylbenzene (1:7410);  $\bar{C}$  with  $NaNH_2$  in liq.  $NH_3$  gives (57% yield (11)) phenylacetylene (1:7425);  $\bar{C}$  in alc. contg.  $BF_3/EtOAc$  (12) or in pres. of HCl (1) condenses with itself by loss of 3 HCl yielding 1,3,5-triphenylbenzene (1:7270).]

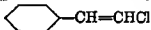
$\bar{C}$  (10 g.) in  $C_6H_6$  (10 ml.) stood 3 days with  $PCl_5$  (30 g.) in  $C_6H_6$  (50 ml.), then poured into aq. worked up as directed (13), yields 1-phenyl-1-chloroethylenephosphinic acid-2,  $C_6H_5-C(Cl)=CH-P(=O)(OH)_2$ , ndls. from dil. HCl, m.p. 162° (13) (together with a little benzoic acid (1:0715), m.p. 121°).

3:8715 (1) Béhal, *Bull. soc. chim.* (2) 50, 632–638 (1888). (2) von Auwers, *Ber.* 45, 2799–2801 (1912). (3) Ley, Rinke, *Ber.* 56, 776 (1923). (4) Urion, Namias, *Bull. soc. chim.* (5) 3, 2335–2336 (1936). (5) Dufraisse, Viel, *Bull. soc. chim.* (4) 37, 878–879 (1925). (6) Taylor, *J. Chem. Soc.* 1937, 304–308. (7) Friedel, *Ann. chim.* (4) 16, 360 (1869). (8) Nef, *Ann.* 308, 269–270 (1898). (9) Perrot, *Compt. rend.* 202, 495 (1936). (10) Vaughn, *J. Am. Chem. Soc.* 56, 2064 (1934). (11) Vaughn, Vogt, Nieuwland, *J. Am. Chem. Soc.* 56, 2121 (1934). (12) Marvel, Moon, *J. Am. Chem. Soc.* 62, 48 (1940). (13) Emerson, Agnew, *J. Am. Chem. Soc.* 67, 518–520 (1945). (14) Emerson (to Monsanto Chem. Co.), U.S. 2,372,562, March 27, 1945; *C.A.* 39, 3555 (1945).

3:8717  $\beta$ -CHLOROVINYLBENZENE $C_6H_7Cl$ 

Beil. V - 476

( $\beta$ -Chlorostyrene,  
 $\omega$ -chlorostyrene, styryl  
 chloride)



$V_1$ -(230)  
 $V_2$ -(367)

B.P.		B.P. (contd.)	
199–100.2°	(1)	02–03° at 22 mm.	(5) $D_4^{25} = 1.1040$ (1)
109°	at 766 mm. (2)	88–100° at 18 mm.	(20) $n_D^{25} = 1.5736$ (1)
197–199°	(3)	83° at 18 mm.	(6) 1.5719 (20)
195.5–190.5° at 715 mm.	(4)	89° at 17 mm.	(7) (1) 1.5700 (20)
113°	at 44 mm. (1)	82–87° at 16 mm.	(20) $D_4^{20} = 1.109$ (9)
112°	at 40 mm. (2)	83–84° at 11 mm.	(8) 1.108 (9)
		79.5° at 11 mm.	(9) $D_4^{15} = 1.1122$ (1)
		78.5° at 9 mm.	(9) $n_D^{15} = 1.5808$ (1)

Liquid with odor of hyacinth; used in perfume industry. Although  $\bar{C}$  should exist in two geom. stereoisomeric forms only this one has as yet been recognized. — Volatile with steam.

[For prepn. of  $\bar{C}$  from cinnamic acid (1:0735) with  $Cl_2$ /aq. or  $HOCl$  (1) (3) (10) (8) (12), with  $Cl_2$  in EtOH (11), with  $NaOCl$  (13) (20), or  $Ca(OCl)_2$  (14) see indic. refs.; from  $\alpha,\beta$ -dichlorohydrocinnamic acid (cinnamic acid dichloride) [Beil. IX-514, IX<sub>1</sub>-(200)] with  $Na_2CO_3$  at 100° (yield: 97% (15) (1)) (9) (6) or with  $NaOAc$  (60% yield (5)) see indic. refs.; from  $\alpha$ -chloro- $\beta$ -hydroxyhydrocinnamic acid [Beil. X-250, X<sub>1</sub>-(110)] by htg. with aq. in s.t. at 200–220° see (2) cf. (3); for formn. of  $\bar{C}$  from  $\omega,\omega$ -dichloroethylbenzene [Beil. V-354] with alc. KOH in s.t. at 120° see (4); from phenyl-trichloromethyl-carbinol [Beil. VI-476, VI<sub>1</sub>-(237)] with Zn dust in alc. see (16); from  $\alpha,\beta$ -dichloroethylbenzene (styrene dichloride) (3:6685) by htg. with pyridine (17) or by passing over  $Al_2O_3$  at 360–400° and 85–105 mm. (92% yield (20)) see indic. refs.; from  $C_6H_5MgBr$  with acetylene tetrachloride (3:5750) see (18); from styrene chlorohydrin (3:9570) by dehydration over  $HPO_3$  on silica gel at 370–400° and 95–115 mm. (63% yield) see (20).

[ $\bar{C}$  with  $Cl_2$  in  $CHCl_3$  yields (1)  $\alpha,\beta$ -trichloroethylbenzene [Beil. V-355], h.p. 254.5–255.5° sl. dec. at 770 mm., h.p. 137° at 21 mm.,  $D_4^{15} = 1.3619$ ,  $n_D^{15} = 1.5652$  (1);  $\bar{C}$  with

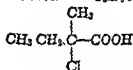
$\text{Br}_2$  in  $\text{CHCl}_3$  yields (1) (13) (19)  $\beta$ -chloro- $\alpha,\beta$ -dibromoethylbenzene [Beil. V-356], ndls. from alc., m.p.  $32^\circ$  (1) (13), b.p.  $165^\circ$  sl. dec. at 26 mm. (1).

$\bar{\text{C}}$  with alc. KOH in s.t. at  $200\text{--}250^\circ$  is partly resinsified (2);  $\bar{\text{C}}$  with very conc. alc. KOH gives on very strong htg. a chlorine-free oil which on distn. with aq. gives phenylacetaldehyde (1:0200) (4). [For rate of loss of halogen with alc. KOH see (5).] —  $\bar{\text{C}}$  with EtOH/NaOEt in s.t. at  $175\text{--}182^\circ$  for  $5\frac{1}{2}$  hrs. gives (66% yield (20))  $\beta$ -ethoxystyrene [Beil. VI-564, VI-(279)] for conversion of which to phenylacetaldehyde see (20).]

$\bar{\text{C}}$  on oxidn. with  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$  or with  $\text{HNO}_3$  ( $D = 1.2$ ) gives (2) benzoic acid (1:0715).

3:8717 (1) Bultz, *Ann.* 296, 266-268, 272-273 (1897). (2) Glaser, *Ann.* 154, 164-167 (1870). (3) Forster, Saville, *J. Chem. Soc.* 121, 2595-2600 (1922). (4) Forster, *Ber.* 17, 982-983 (1884). (5) Dann, Howard, Davies, *J. Chem. Soc.* 1928, 609-610. (6) Durrans, *J. Chem. Soc.* 123, 1427 (1923). (7) Bergmann, *J. Chem. Soc.* 1936, 404. (8) Farmer, Hose, *J. Chem. Soc.* 1933, 964. (9) von Auwers, *Ber.* 45, 2796-2797 (1912). (10) Erlenmeyer, Lipp, *Ann.* 219, 185-186 (1883). (11) Jackson, Pasiut, *J. Am. Chem. Soc.* 49, 2074 (1927). (12) Böeseken, *Rec. trav. chim.* 41, 204 (1921). (13) Ssuknewitsch, *Tschilingarjan, Ber.* 63, 1214 (1935). (14) Stenhouse, *Ann.* 55, 3-4 (1845). (15) Erlenmeyer, *Ber.* 14, 1868 (1881). (16) Jonisch, Favorski, *J. Russ. Phys.-Chem. Soc.* 30, 920-924 (1898), *Cent.* 1899, I 607. (17) I.G., French 729,730, July 30, 1932; *Cent.* 1932, II 3015. (18) Swarts, *Bull. soc. chim.* (4) 25, 168-169 (1919). (19) Reich, van Wijck, Waelle, *Helv. Chim. Acta* 4, 248 (1921). (20) Emerson, Agnew, *J. Am. Chem. Soc.* 67, 518-520 (1945).

3:8718 *d,l*- $\alpha$ -CHLORO- $\alpha$ -METHYL-*n*-BUTYRIC ACID  $\text{C}_4\text{H}_7\text{O}_2\text{Cl}$  Beil. II-306



$\text{H}_1\text{—}$   
 $\text{H}_2\text{—}$

B.P.  $200\text{--}205^\circ$  at 754 mm., sl. dec. (1)  
 $123\text{--}124^\circ$  at 36 mm. (1)

$D_4^{20} = 1.101$  (1)  $n_D^{25} = 1.45077$  (1)

Only liq.; insol. aq.; sol. alc., ether.

[For prepn. of  $\bar{\text{C}}$  from  $\alpha$ -chloro- $\alpha$ -methyl-*n*-butyronitrile by hydrolysis with conc. HCl see (1).]

- Methyl  $\alpha$ -chloro- $\alpha$ -methyl-*n*-butyrate: unreported.
- Ethyl  $\alpha$ -chloro- $\alpha$ -methyl-*n*-butyrate (see 3.8518).
- $\alpha$ -Chloro- $\alpha$ -methyl-*n*-butyramide: unreported.
- $\alpha$ -Chloro- $\alpha$ -methyl-*n*-butyranilide: unreported.
- $\alpha$ -Chloro- $\alpha$ -methyl-*n*-butyro-*p*-toluidide: unreported.

3:8718 (1) Servais, *Rec. trav. chim.* 20, 58-59 (1901).

3:8719 1-CHLORONONANE  $\text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{Cl}$   $\text{C}_9\text{H}_{19}\text{Cl}$   
(*n*-Nonyl chloride)

Beil. I —  
 $\text{I}_1\text{—}$   
 $\text{I}_2\text{—}(128)$

B.P.

$202^\circ$  at 760 mm. (4)

$98\text{--}100^\circ$  at 22 mm. (1)

$92.6\text{--}93.0^\circ$  at 16 mm. (2)

$76\text{--}79^\circ$  at 4 mm. (3)

$D_4^{25} = 0.8031$  (3)

$D_{20}^{20} = 0.8679$  (1)

$D_4^{20} = 0.8704$  (4)

$n_D^{25} = 1.4400$  (3)

$n_D^{20} = 1.43692$  (1)

1.43400 (4)

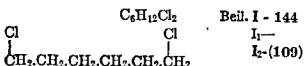
[For prepn. of  $\bar{\text{C}}$  from nonanol-1 (1:6265) +  $\text{PCl}_3$  +  $\text{ZnCl}_2$  (53% yield) or  $\text{PCl}_5$  +  $\text{ZnCl}_2$  in  $\text{C}_6\text{H}_6$  (55% yield) or excess  $\text{SOCl}_2$  (76% yield (4)) in  $\text{C}_6\text{H}_6$  (62% yield) see (1);



for prepn. of  $\bar{C}$  (52% yield (3)) from *n*-hexyl MgBr +  $\gamma$ -chloro-*n*-propyl *p*-toluenesulfonate see (3).]

3:8719 (1) Clark, Streight, *Trans. Roy. Soc. Can.* (3) 23, III 77-89 (1929). (2) Kohlrausch, Koppl, *Monatsh.* 63, 269 (1933). (3) Rossander, Marvel, *J. Am. Chem. Soc.* 50, 1495 (1928). (4) Vogel, *J. Chem. Soc.* 1943, 638, 640.

3:8720 1,6-DICHLOROHEXANE  
(Hexamethylene dichloride)



B.P. 203-205° (1)

94° at 22 mm. (2)

[For prepn. of  $\bar{C}$  from *N,N'*-bis-benzoylhexamethylenediamine [Beil. IX-263] via reactn. with  $\text{PCl}_5$  and distn. of the resultant bis-(amide chloride) (64% yield (2)), or similarly from *N*-(benzoyl)hexamethyleneimine [Beil. XX<sub>1</sub>-(27)] (3), see (2) (3); for formn. from hexamethylenediamine [Beil. IV-269] with  $\text{NOCl}$  (1) or from hexanediol-1,6 diphenyl ether [Beil. VI-148] by htg. with  $\text{HCl}$  in a.t. at 165-175° see (1).]

⑥ Hexanediol-1,6 diphenyl ether (1,6-diphenoxyhexane) [Beil. VI-148]: cryst. from alc., m.p. 83° (2), 83.0-83.6° cor. (3). [From  $\bar{C}$  on refluxing 12½ hrs. with large excess sodium phenolate in alc. (2) (41% yield (3))]. [The half reactn. prod.,  $\omega$ -chloro-*n*-hexyl phenyl ether [Beil. VI-144], is an oil, b.p. 164-165° at 11 mm. (4).]

3:8720 (1) Solonina, *J. Russ. Phys.-Chem. Soc.* 30, 606-632 (1898); *Cent.* 1899, I 25. (2) von Braun, *Ber.* 38, 2344-2345 (1905). (3) Müller, Sauerwald, *Monatsh.* 48, 732 (1927). (4) von Braun, Müller, *Ber.* 39, 4112-4113 (1906).

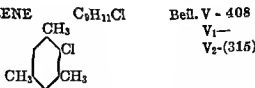
—  $\beta$ -CHLOROPROPIONIC ACID  $\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$   $\text{C}_3\text{H}_5\text{O}_2\text{Cl}$  Beil. II - 249  
 $\text{II}_1-(111)$   
 $\text{II}_2-(226)$

B.P. 204°

M.P. 42°

See 3:0460. Division A: Solids.

3:8725 2-CHLORO-1,3,5-TRIMETHYLBENZENE  
(*eso*-Chloromesitylene)



B.P. 204-206° (1)

103.6-103.7° at 25 mm. (2)

90-91° at 20 mm. (3)

$D_4^{20} = 1.0337$  (2)  $n_D^{20} = 1.52119$  (2)

$\bar{C}$  remains liquid down to  $-20^\circ$ .  $\bar{C}$  is insol. aq., eas. sol. alc. or ether; volatile with steam but less so than dichloromesitylene.

[For prepn. of  $\bar{C}$  from 1,3,5-trimethylbenzene (mesitylene) (1:7455) with  $\text{Cl}_2$  either directly (1) or in  $\text{CHCl}_3$  at  $0^\circ$  (75% yield (3)) accompanied by 2,4-dichloro-1,3,5-trimethylbenzene (1) and/or 2,4,6-trichloro-1,3,5-trimethylbenzene, m.p. 209° (3), 204-205° (1), or from 2,4,6-trimethylphenol (mesitol) (1:1467) with  $\text{PCl}_5$  in  $\text{C}_6\text{H}_6$  (2) see indic. refs.]

$\bar{C}$  with fuming  $\text{H}_2\text{SO}_4$  (20%  $\text{SO}_3$ ) shaken for 15 min. gives 2-chloromesitylenesulfonic acid

(corresp. sulfonyl chloride, oil (3), sulfonamide, m.p. 165.5-166° (3)) but gives no evidence of any Jacobsen rearrangement (3).

$\bar{C}$  with fuming  $HNO_3$  yields (1) (4) mainly 4,6-dinitro-2-chloromesitylene, colorless ndls. from alc., m.p. 178-179° (1), 176.5° (4) [the mononitration prod., 4-nitro-2-chloromesitylene, has m.p. 56-57° (1)].

$\bar{C}$  on oxidn. with boilg. dil.  $HNO_3$  (1 conc.  $HNO_3$ : 2 aq.) for 30 hrs. yields (1) 4-chloro-3,5-dimethylbenzoic acid ("chloromesitylenic acid") [Beil. IX-536], browns at 220° but does not melt (unsuitable as derivative). [Note that a little 4-nitro-2-chloromesitylene m.p. 56-57° (1), may be formed in this process; furthermore that attempts to oxidize  $\bar{C}$  with  $K_2Cr_2O_7$  + dil.  $H_2SO_4$  yield only acetic acid (1).]

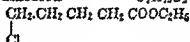
$\bar{C}$  on oxidn. with aq.  $KMnO_4$  gives (63.5% yield (5)) 2-chlorobenzenetricarboxylic acid-1,3,5 (chlorotrimelic acid) (3:4975), readily sol. cold aq., excessively sol. hot aq., m.p. anhydrous acid 285° (5), monohydrate 278° (6).

3:8725 (1) Fittig, Hoogewerff, *Ann.* 150, 323-329 (1869). (2) Brown, de Bruyne, Gross, *J. Am. Chem. Soc.* 56, 1291 (1934). (3) Smith, Moyle, *J. Am. Chem. Soc.* 58, 1, 4, 7 (1936). (4) Anschutz, Boedeker, *Ann.* 454, 108 (1927). (5) Davies, Wood, *J. Chem. Soc.* 1928, 1126-1127. (6) Ost, *J. prakt. Chem.* (2) 15, 310 (1877).

### 3:8727 ETHYL $\delta$ -CHLORO-*n*-VALERATE

 $C_7H_{13}O_2Cl$ 

Beil. II - 302


 $\Pi_1$ —  
 $\Pi_2$ -(268)

B.P. 205-206° (1)  
 120-125° at 40 mm. (2)  
 93° at 16 mm. (5)  
 83.5-85° at 8 mm. (4)  
 83° at 8 mm. (3)

 $n_D^{20} = 1.4355$  (4)

[For prepn. of  $\bar{C}$  from  $\delta$ -chloro-*n*-valeric acid (3:0075) with EtOH + dry HCl see (1) (2) (3) (4); from  $\delta$ -ethoxy-*n*-valeryl chloride (5) on htg. with 0.7% conc.  $H_2SO_4$  at 100° for 5 hrs see (5).]

[For reactn. of  $\bar{C}$  with diethyl sodio-ethylmalonate see (2); for rate of reactn. of  $\bar{C}$  with KI in acetone at 50° see (3).]

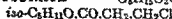
Neither  $\bar{C}$  nor its halogen is rapidly hydrolyzed by cold aq. 10% NaOH (3) (use in sepn. of  $\bar{C}$  from phenol (3)).

3:8727 (1) Funk, *Ber.* 26, 2574-2575 (1893). (2) Mellor, *J. Chem. Soc.* 79, 132 (1901). (3) Conant, Kirner, *J. Am. Chem. Soc.* 46, 244-245, 249 (1924). (4) Cheney, Piening, *J. Am. Chem. Soc.* 67, 733 (1945). (5) Prelog, Heimbach-Juhász, *Ber.* 74, 1704 (1941).

### 3:8730 ISOAMYL $\beta$ -CHLOROPROPIONATE

 $C_8H_{17}O_2Cl$ 

Beil. II —


 $\Pi_1$ -(111)  
 $\Pi_2$ -(227)

B.P. 207-208° at 740 mm. (1)  
 121° at 30 mm. (4)  
 87° at 12 mm. (2)

 $D_4^{20} = 1.0171$  (3)

 $n_D^{20} = 1.4343$  (3)

 $D_4^{15} = 1.0419$  (4)

 $n_D^{11} = 1.4380$  (4)

[For prepn. (97% yield (2), 90% yield (1)) from isoamyl alc. (1:6200) +  $\beta$ -chloropropionic ac. (3:0460) see (1) (2).]

$\bar{C}$  on htg. at 220° with diethylaniline gives (poor yield (4)) isoamyl acrylate, b.p. 157-159° at 756 mm.,  $n_D^{15} = 1.4287$  (4).

① Isoamyl  $\beta$ -(phthalimido)propionate: from  $\bar{C}$  in 70% yield on btg. with potassium phthalimide in s.t. at 130° for 1 hr.; prod. repeatedly extracted with dry ether and solvent evapd.; cryst. from alc., m.p. 61° (1). [This product on shaking with 12 pts. HBr (48%) at 40° yields  $\beta$ -phthalimidopropionic acid (40% yield), cryst. from aq., m.p. 150-151° (4).]

3:8730 (1) Hale, Britton, *J. Am. Chem. Soc.* **41**, 844-845 (1919). (2) Fichter, Schnider, *Helv. Chim. Acta* **14**, 857 (1931). (3) Schjanberg, *Z. physik. Chem. A*-**172**, 231 (1935). (4) Moureu, Murat, Tampier, *Ann. chim.* (9) **15**, 247, 251 (1921).

3:8735 *o*-CHLOROPHENETOLE  
(*o*-Chlorophenyl ethyl ether)



Beil. VI - 184  
VI—

B.P. 210.3° (1)  
208° (2)  
97-98° at 15 mm. (5)

$D_4^{25} = 1.1288$  (5)  
 $D_{44}^{24.2} = 1.12993$  (1)

$n_D^{25} = 1.5284$  (5)  
 $n_{H_A}^{24.2} = 1.52333$  (1)  
 $n_{H_B}^{24.2} = 1.54014$  (1)

Colorless oil, volatile with steam.

[For prepn. from 3-chloro-4-ethoxyaniline [Beil. XIII-511, XIII<sub>1</sub>-(181)] by replacement of  $-NH_2$  group with H via diazo reaction see (3).]

$\bar{C}$  added dropwise to 2 pts.  $HNO_3$  ( $D = 1.38$ ) with cooling, then poured into aq., yields (3) 2-chloro-4-nitrophenetole [Beil. VI-240], yel. ndls. from alc. + lgr., m.p. 82° (3).

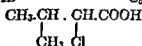
② 3-Chloro-4-ethoxybenzenesulfonamide: cryst. from dil. alc., m.p. 132-133° u.c. (4). [From  $\bar{C}$  by treatment with chlorosulfonic ac. followed by conversion of the intermediate sulfonyl chloride to the sulfonamide by treatment with  $(NH_4)_2CO_3$  (73% yield (4)).] [Note that this prod. depresses the m.p. of the corresponding deriv. (m.p. 134-134.5°) from *p*-chlorophenetole (3:0090) (4).]

3:8735 (1) Swarts, *J. chim. phys.* **20**, 75-76 (1923). (2) Beilstein, Kurbatow, *Ann.* **176**, 39 (1875). (3) Reverdin, Düring, *Ber.* **32**, 155-156 (1899). (4) Huntress, Carten, *J. Am. Chem. Soc.* **62**, 603-604 (1940). (5) Anzilotti, Curran, *J. Am. Chem. Soc.* **65**, 609 (1943).

— *d,l*- $\alpha$ -CHLORO-ISOVALERIC ACID



Beil. II - 316



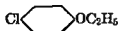
II<sub>1</sub>—  
II<sub>2</sub>—

B.P. 210-212° at 756 mm. M.P. 16°  $D_4^{13.2} = 1.135$

$n_D^{11} = 1.44496$

See 3:0050. Division A: Solids.

— *p*-CHLOROPHENETOLE



Beil. VI - 187  
VI<sub>1</sub>-(101)  
VI<sub>2</sub>-(176)

B.P. 211.6° cor.

M.P. 20-21°

$D_{20.2}^{20.2} = 1.12310$

$n_D^{19} = 1.5227$

See 3:0090. Division A: Solids.

—  $\alpha$ -CHLOROCROTONIC ACID

$$\begin{array}{c} \text{CH}_3-\text{C}-\text{H} \\ \parallel \\ \text{Cl}-\text{C}-\text{COOH} \end{array}$$

$\text{C}_4\text{H}_5\text{O}_2\text{Cl}$


Beil. II - 414  
II<sub>1</sub>-(189)  
II<sub>2</sub>-(395)

B.P. 212°

M.P. 99-100°

See 3:2760. Division A: Solids.

3:8737 1-CHLORO-3-PHENYLPROPENE-1  
( $\omega$ -Chloroallylbenzene;  
 $\gamma$ -chloroallylbenzene)



$\text{C}_9\text{H}_9\text{Cl}$

Beil. V —  
V<sub>1</sub>—  
V<sub>2</sub>-(373)

B.P. 212-214° cor. (1)  
97° at 18 mm. (1)  
76° at 13 mm. (2)

$D_4^{14} = 1.073$  (1)

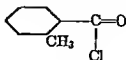
$n_D^{14} = 1.545$  (1)

Liquid with penetrating odor suggesting benzene.  
[For prepn. of  $\bar{C}$  from 1,3-dichloropropene-1 (3:5280) with  $\text{C}_6\text{H}_6 + \text{AlCl}_3$  (3), or with  $\text{C}_6\text{H}_5\text{MgBr}$  in toluene (1) (4) or ether (2) (alm. quant. yield (1)), see indic. refs.]  
 $\bar{C}$  with  $\text{PCl}_5$  gives on warming (by addition to  $\bar{C}$  of 2 atoms chlorine) alm. quant. yield (5) of 3-phenyl-1,1,2-trichloropropene, b.p. 135-136° at 13 mm.,  $D_4^{23} = 1.293$ ,  $n_D^{23} = 1.553$  (5).  
 $\bar{C}$  with  $\text{Br}_2$  adds similarly giving (1) (4) 1-chloro-1,2-dibromo-3-phenylpropane, b.p. 160° at 12 mm.,  $D_4^{10} = 1.727$ ,  $n_D^{10} = 1.611$  (4) (for use of this prod. in prepn. of hydrocinnamaldehyde (1:0225) see (6)).  
[ $\bar{C}$  resists hydrolysis and is unchanged even after several hours with aq. +  $\text{PbO}$  in s.t. at 200° (1) (4); however,  $\bar{C}$  with  $\text{KOH}$  (3 moles) in abs. alc. on refluxing at 130-135° is readily converted (by reactn. of the  $\omega$ -chlorine atom and rearr. or vice versa) into cinnamyl ethyl ether ( $\gamma$ -ethoxyallylbenzene) (Beil. VI-571, VI<sub>1</sub>-(281)], b.p. 127-128° at 22 mm.,  $D_4^{13} = 0.970$ ,  $n_D^{13} = 1.547$  (1) (4), which by cleavage with  $\text{HCl}$  under press. gives (7) cinnamyl chloride (3:0010) q.v.]  
[ $\bar{C}$  with  $\text{Na}$  (4 moles) in boilg. toluene gives (8) propenylbenzene ( $\beta$ -methylstyrene) (Beil. V-481, V<sub>1</sub>-(371)], b.p. 176°, neither methyl phenylacetylene nor benzylacetylene being formed.]  
[ $\bar{C}$  with  $\text{NaNH}_2$  in high-boilg. pet. at 105-110° gives (75% yield (9)) (10) (11) benzylacetylene (Beil. V<sub>2</sub>-(408)], b.p. abt. 166° at 760 mm. (with resinification).]

3:8737 (1) Bert, *Bull. soc. chim.* (4) 37, 879-881 (1925). (2) von Braun, Kuhn, *Ber.* 58, 2171 (1925). (3) Bert, *Compt. rend.* 213, 619-620 (1941); *Cent.* 1942, II 30-31; *C.A.* 37, 4373 (1943). (4) Bert, *Compt. rend.* 180, 1504-1506 (1925). (5) Bert, *Anniquin, Compt. rend.* 192, 1107-1108 (1931). (6) Bert, *Compt. rend.* 215, 356-357 (1942); *C.A.* 38, 3633 (1944). (7) Bert, Dorier, t. Raynaud, bert, Dorier, 193 (1927).

## 3:8740 o-TOLUYL CHLORIDE

(o-Methylbenzoyl chloride)

 $\text{C}_8\text{H}_7\text{OCl}$ 

Beil. IX - 464

IX<sub>1</sub>-(187)

B.P.

213.0-213.6° at 760 mm. (1)

213° at 760 mm. (2)

212° at 762 mm. (3)

212° cor. (4)

211° at 733 mm. (5)

206-208° (6)

B.P. (contd.)

110-111° at 29 mm. (7)

109-123° at 28 mm. (8)

99-100° at 12 mm. (9)

99-103° at 11 mm. (10)

83° at 8 mm. (26)

75.6° at 5.5 mm. (11)

75.0-75.5° at 2 mm. (12)

[For prepn. of  $\bar{\text{C}}$  from o-toluic acid (1:0690) with  $\text{PCl}_5$  (10) (yield: 100% (3), 75% (13)), with  $\text{PCl}_5$  in  $\text{CHCl}_3$  (7), with  $\text{PCl}_3$  at 110° (14), with  $\text{POCl}_3$  (6) or  $\text{POCl}_3$  + alk. chloride (15), with  $\text{SOCl}_2$  (11) (yield: 100% (9), 95% (2), 92% (26), 89% (4)) see indic. refs.; for prepn. of  $\bar{\text{C}}$  from o-toluic anhydride (see below) with  $\text{PCl}_5$  in  $\text{POCl}_3$  see (7).]

$\bar{\text{C}}$  with pyridine + excess  $\text{K}_2\text{S}_2\text{O}_5$  yields (16) o-toluic anhydride, m.p. 39° (16) (7), 36-37° (17).

[For Friedel-Crafts reactn. of  $\bar{\text{C}}$  +  $\text{AlCl}_3$  + various hydrocarbons to yield corresp. ketones, e.g., with  $\text{C}_6\text{H}_6$  (5) (6) (18), with toluene (19), with naphthalene (9), with phenanthrene (20), with acenaphthene (4), etc., see indic. refs.;  $\bar{\text{C}}$  with  $\text{MeZnI}$  gives (75% yield (21)) methyl o-tolyl ketone.]

[For studies of rate of reactn. of  $\bar{\text{C}}$  with  $\text{MeOH}$  (22) (23), with  $\text{EtOH}$  (12) see indic. refs.]

[For actn. of  $\text{Br}_2$  on  $\bar{\text{C}}$  see (2); for reactn. of  $\bar{\text{C}}$  with diethyl sodiomalonate see (24); for sulfonation of  $\bar{\text{C}}$  see (25); for behavior of  $\bar{\text{C}}$  with  $\text{C}_6\text{H}_5\text{MgBr}$  in ether +  $\text{CoBr}_2$  see (26).]

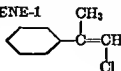
$\bar{\text{C}}$  on hydrolysis yields o-toluic acid (1:0690), m.p. 104° (for the amide, anilide, p-toluidide, and other derivatives corresp. to  $\bar{\text{C}}$  see 1:0690).

3:8740 (1) Kohlrausch, Pongratz, Stockmair, *Monatsh.* 67, 107 (1936). (2) Davies, Perkin, *J. Chem. Soc.* 121, 2207 (1922). (3) van Scherpenzeel, *Rec. trav. chim.* 20, 169 (1901). (4) Guyer, Zuffanti, *J. Am. Chem. Soc.* 57, 1787-1788 (1935). (5) Ador, Fillet, *Ber.* 12, 2301 (1879). (6) Reddellien, *Ber.* 48, 1468 (1915). (7) Klages, Lackroth, *Ber.* 32, 1561 (1889). (8) Hayashi, *J. prakt. Chem.* (2) 123, 300 (1929). (9) Mayer, Fleckenstein, Gunther, *Ber.* 63, 1470 (1930). (10) Cohen, Dudley, *J. Chem. Soc.* 97, 1740 (1910).

(11) Thompson, Norris, *J. Am. Chem. Soc.* 58, 1955 (1936). (12) Norris, Young, *J. Am. Chem. Soc.* 57, 1420-1424 (1935). (13) Tanner, Lasselle, *J. Am. Chem. Soc.* 48, 2164 (1926). (14) Frankland, Wharton, *J. Chem. Soc.* 69, 1311 (1896). (15) Kissling (to I.G.), *Ger.* 642,519, March 10, 1937; *Cent.* 1937, I 3874; *C.A.* 31, 5816 (1937). (16) Gasopoulos, *Praktika Acad. Athnon* 6, 347-353 (1931). (17) Adams, Wirth, French, *J. Am. Chem. Soc.* 40, 426 (1918). (18) Diesbach, Strebel, *Helv. Chim. Acta* 8, 561 (1925). (19) Mauthner, *J. prakt. Chem.* (2) 103, 393 (1921). (20) Clar, *Ber.* 62, 358 (1929).

(21) Ruzicka, Ehmann, *Helv. Chim. Acta* 15, 150 (1932). (22) Norris, Fasce, Staud, *J. Am. Chem. Soc.* 57, 1415-1420 (1935). (23) Ott, *Ber.* 55, 2123 (1922). (24) Mercer, Robertson, *J. Chem. Soc.* 1936, 292. (25) Meiser (to General Aniline and Film Corp.), U.S. 2,273,974, Feb. 24, 1942; *C.A.* 36, 3809 (1942). (26) Kharasch, Nudenberg, Archer, *J. Am. Chem. Soc.* 65, 497 (1943).

## 3:8742 1-CHLORO-2-PHENYLPROPENE-1

( $\beta$ -Chloro- $\alpha$ -methylstyrene) $\text{C}_9\text{H}_7\text{Cl}$ 

Beil. V - 485

V<sub>1</sub>-V<sub>2</sub>-

B.P. 213-215° (1)

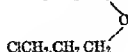
210-215° (2)

102-106° at 14 mm. (2)

[For prepn. of  $\bar{C}$  from  $\alpha,\beta$ -dichloroisopropylbenzene ( $\alpha$ -methylstyrene dichloride) [Beil. V-395] with alc. KOH see {2}; from  $\beta$ -chloro- $\alpha$ -hydroxyisopropylbenzene [Beil. VI-507] on distn. at ord. press. {3} or by htg with oxalic acid {2} see indic. refs.; from the lower-melting stereoisomer of  $\beta$ -methylcinnamic acid [Beil. IX-614, IX-(254)] with HOCl see {2}.]

3:8742 {1} Tiffeneau, *Compt. rend.* 133, 986 (1904). {2} Tiffeneau, *Ann. chim.* (8) 10, 166, 173, 180 (1907). {3} Tiffeneau, *Compt. rend.* 134, 775 (1902).

3:8745  $\gamma,\gamma'$ -DICHLORO-DI-*n*-PROPYL ETHER  $C_6H_{12}OCl_2$  Beil. S.N. 24  
(bis-( $\gamma$ -Chloro-*n*-propyl)ether)  $ClCH_2CH_2CH_2$



B.P. 215° at 745 mm. {1}  
93-95° at 12 mm. {2}

$D_{20}^{20} = 1.140$  {1}

[For prepn. (10-15% yield {1}) from trimethylene chlorohydrin (3:8285) by refluxing with dil.  $H_2SO_4$  see {1}.]

3:8745 {1} Kamm, Newcomb, *J. Am. Chem. Soc.* 43, 2228-2229 (1921). {2} Eastman Org. Chem. List No. 23 (1942).

3:8765 PELARGONYL CHLORIDE  $CH_3(CH_2)_7C(=O)Cl$   $C_9H_{17}OCl$  Beil. II - 353'  
(*n*-Nonanoyl chloride)  $\begin{array}{c} \diagup \\ C=O \\ \diagdown \\ Cl \end{array}$   $\begin{array}{c} H_1- \\ H_2- \\ H_3-(308) \end{array}$

B.P.

F.P.

215-35° at 760 mm. {1}

-60.5° {1}

$D_4^{25} = 0.93780$  {1}

220° at 749 mm. {2}

$D_4^{20} = 0.94206$  {1}

98° at 15 mm. {3}

$D_4^{15} = 0.94633$  {1}  $n_{D,20}^{15} = 1.43802$  {1}

93-96° at 11 mm. {4}

89° at 6 mm. {5}

[For prepn. of  $\bar{C}$  from pelargonic acid (*n*-nonanoic acid) (1:0560) with  $PCl_5$  {3} (65% yield {6}), with  $PCl_3$  {2} (72% yield {1}), with  $PCl_3 + ZnCl_2$  (93% yield {6}), or with  $SOCl_2$  (yield 93.5% {4}, 85% {6}) see indic. refs.]

[For reactn. of  $\bar{C}$  with toluene +  $AlCl_3$  to give corresp. ketone see {7}, with  $AlCl_3$  + anisole to give corresp. ketone see {8}, with ethyl sodio-acetoacetate and hydrolysis to methyl *n*-octyl ketone (decanone-2) see {9}, with K carbazole to yield *N*-(*n*-nonyl)carbazole, m.p. 72-73°, see {10}, with vanillylamine see {5}.]

[ $\bar{C}$  with  $AlCl_3$  + phenol yields {11} 55% *o*-(*n*-nonanoyl)phenol, b.p. 180° at 10 mm., m.p. 18.4°,  $D_4^{24} = 0.9857$ ,  $n_D^{25} = 1.5139$  {11} (semicarbazone, m.p. 164° {11}), and 35% *p*-(*n*-nonanoyl)phenol, m.p. 54.5°, b.p. 232° at 10 mm. (benzoate, m.p. 99.8° {11}).]

$\bar{C}$  on hydrolysis yields pelargonic acid (1:0560) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresp. to  $\bar{C}$  see 1:0560).

3:8765 {1} Delfet, *Bull. soc. chim. Belg.* 40, 359-396 (1931). {2} Henry, *Bull. acad. roy. Belg.* (3) 27, 63-72 (1899); *Cent.* 1899, 1 968; *Rec. trav. chim.* 18, 253-254 (1899). {3} Kraft, Koenig, *Ber.* 23, 2384 (1890). {4} Fierz-David, Kuster, *Helv. Chim. Acta* 22, 86-89 (1939). {5} Ford-Moore, Phillips, *Rec. trav. chim.* 53, 855 (1934). {6} Clark, Bell, *Trans. Roy. Soc. Can.* (3) 27, 111 97-103 (1933). {7} Hasan, Stedman, *J. Chem. Soc.* 1931, 2117. {8} Skraup, Nieten, *Ber.* 57, 1302-1303 (1924). {9} Asahina, Nakayama, *J. Pharm. Soc. Japan* 1925, No. 526, 3-5; *Cent.* 1925, 1 2670. {10} Copisarow, *J. Chem. Soc.* 113, 818 (1915).

{11} Sandulesco, Girard, *Bull. soc. chim.* (4) 47, 1310 (1930).

— *p*-CHLOROBENZALDEHYDE ClC1=CC=CC=C1C=O  $C_7H_5OCl$  Beil. VII - 235  
 VII<sub>1</sub>-(133)  
 B.P. 214.5°-216.5° at 760 mm. M.P. 48-49°

See 3:0765. Division A: Solids.

3:8770 3-CHLORO-4-ISOPROPYL-1-METHYLBENZENE  $C_{10}H_{13}Cl$  Beil. V - 423  
 (3-Chloro-*p*-cymene) (CH3)2CHC1=CC=C(C=C1)C V<sub>1</sub>—  
 V<sub>2</sub>-(326)  
 Cl

B.P. 217.1° at 760 mm. (1)  $D_4^{18} = 1.01799$  (5)  
 213-214° cor. at 735.6 mm. (2)  $n_D^{18} = 1.51796$  (5)  
 214° at 760 mm. (3)  
 120-122° at 20 mm. (4) (5)

[For prepn. of  $\bar{C}$  from thymol (3-hydroxy-*p*-cymene) (1:1430) with  $PCl_5$  see (1) (4) (5) (6); for prepn. of  $\bar{C}$  from 2-bromo-*p*-cymene [Beil. V-423, V<sub>1</sub>-(205)] by chlorination to 5-chloro-2-bromo-*p*-cymene [Beil. V-424] followed by replacement of Br by H with Zn/Cu at 200° (7) or in alc. alk. (8) see (7) (8); for prepn. of  $\bar{C}$  from 3-chloromenthadiene dibromide by elimination of 2 HBr with quinoline see (3).]

[ $\bar{C}$  on oxidn. with 15 pts. hoilg. dil.  $HNO_3$  ( $D = 1.24$ ) gives (2) a mixt. of 3-chloro-4-isopropylbenzoic acid (3-chlorocuminic acid) [Beil. IX-549], m.p. 122-123°, 2-chloro-4-methylbenzoic acid (2-chloro-*p*-toluic acid) (3:4355), m.p. 155°, and 2-chloroterephthalic acid (3:4995), m.p. about 320°.]

[ $\bar{C}$  on mononitration with 6 pts. conc.  $HNO_3$  ( $D = 1.48$ ) below 15° for 3-4 hrs. as directed (4) yields 6-nitro-3-chloro-*p*-cymene = 2-nitro-5-chloro-*p*-cymene [Beil. V-424], oil, b.p. 142-150° at 13 mm. (4) (which with piperidine for 30 min. at 100° yields (4) 2-nitro-5-piperidino-*p*-cymene, oil, b.p. 146-148° at 32 mm. (4)).]

$\bar{C}$  on dinitration by adding to 10 pts. conc.  $HNO_3$  ( $D = 1.5$ ) below -5° during 15 min., then poured onto ice, yields (4) (9) a mixt. from which can be isolated 2,6-dinitro-3-chloro-*p*-cymene, m.p. 105-106° (9), 102.5-103.5° (4) (which with piperidine (5 pts.) at 100° for 1½ hrs. yields 2,6-dinitro-3-piperidino-*p*-cymene, pale yel. ndls. from alc., m.p. 126-127° (9), 123-124° (4)).

[During this dinitration of  $\bar{C}$  there is also formed a by-prod. formerly (4) supposed to be 2-chloro-3,5-dinitro-4-methylacetophenone but more recently (10) shown to be 3-chloro-4,6-dinitrotoluene, m.p. 90.0-90.5° (10); this prod. with piperidine gives (10) 3-piperidino-4,6-dinitrotoluene, m.p. 116-116.5° (10).]

3:8770 (1) Kobe, Okabe, Ramstad, Huemmer, *J. Am. Chem. Soc.* **63**, 3251-3252 (1941). (2) Fileti, Crosa, *Gazz. chim. ital.* **16**, 288 (1886). (3) Junger, Klages, *Ber.* **29**, 316 (1896). (4) Ganguly, R. J. W. LeFevre, *J. Chem. Soc.* **1934**, 848-852. (5) C. G. LeFevre, R. J. W. LeFevre, K. W. Robertson, *J. Chem. Soc.* **1935**, 483. (6) Vongerichten, *Ber.* **11**, 364-369 (1878). (7) ———, *ibid.* **12**, 177-181 (1879). (8) Livak, Carlson, (9) Qvist, Moilanen, *Acta Chem. Scand.*, II 1337-1338; *C.A. Abs.* **14**, No. 3, 9 pp.

at 180-200° see (1); from 1,6-dichloronaphthalenesulfonyl chloride-3 [Beil. XI-182] (14) or from 1,6-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-163] (18) by hgt. with conc. HCl in s.t. at 290° see indic. refs., from sodium  $\alpha$ -naphthalenesulfonate [Beil. XI-155, XI-1-37] with boilg. dil. HCl + KClO<sub>3</sub> (other products are also formed) see (15).]

[C on mononitration in AcOH with fumg. HNO<sub>2</sub> yields (19) (20) 1,6-dichloro-4-nitronaphthalene [Beil. V-556], m.p. 119° (19).]

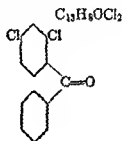
[C on monosulfonation with mixt. of equal vols. conc. + fumg. H<sub>2</sub>SO<sub>4</sub> (17) or with ClSO<sub>3</sub>H in CS<sub>2</sub> (18) gives 1,6-dichloronaphthalenesulfonic acid-4 [Beil. XI-163] (corresp. sulfonyl chloride, m.p. 151° (17) (18), corresp. sulfonamide, m.p. 216° (18)).]

[C on oxida. with dil. HNO<sub>3</sub> in s.t. at 150° yields (19) a mixt. of 3-chlorophthalic acid (3.4820) and 4-chlorophthalic acid (3.4390) together with their nitro derivs.]

3:0810 (1) Friedländer, Kielbasinski, *Ber.* 29, 1980-1992 (1896). (2) Schroeter, *Ber.* 63, 1318 (1930). (3) Hampson, Weissberger, *J. Chem. Soc.* 1936, 394. (4) Forsling, *Ber.* 20, 2105 (1887). (5) Erdmann, Kirchhoff, *Ann.* 247, 379 (1888). (6) Ferrero, Bolliger, *Helv. Chim. Acta* 11, 1146-1150 (1926). (7) Armstrong, Wynne, *Chem. News* 71, 255 (1895). (8) Sindall, *Chem. News* 60, 58 (1889). (9) Cleve, *Bull. soc. chim.* (2) 26, 448 (1876). (10) Armstrong, Wynne, *Chem. News* 62, 164 (1890).

(11) Erdmann, *Ann.* 275, 214-215, 256, 279 (1893). (12) Friedländer, Szymanski, *Ber.* 25, 2081 (1892). (13) Kehrman, Matis, *Ber.* 31, 2419 (1898). (14) Armstrong, Wynne, *Chem. News* 76, 69 (1897). (15) Kozlov, Talybov, *J. Gen. Chem. (U.S.S.R.)* 9, 1827-1833 (1939); *C.A.* 34, 4067 (1940). (16) Zil'berman, Rashevskaya, Martynseva, *J. Applied Chem. (U.S.S.R.)* 9, 1832-1840 (1936), *Cent.* 1937, 1 4787, *C.A.* 31, 2597 (1937). (17) Cleve, *Ber.* 24, 3177-3478 (1891). (18) Armstrong, Wynne, *Chem. News* 61, 274-275 (1890). (19) Cleve, *Bull. soc. chim.* (2) 29, 499 (1878). (20) Armstrong, Wynne, *Chem. News* 61, 94 (1890).

3:0825 2,4-DICHLOROBENZOPHENONE  
(2,4-Dichlorophenyl phenyl  
ketone)



Beil. VII - 420  
VII—

M.P. 48-49° (1) (2)  
52° (3)

Cryst. (from alc. (1)).

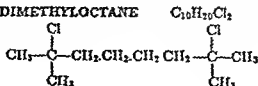
{For prepn. from *m*-dichlorobenzene (3:5960) + BzCl (3:6240) + AlCl<sub>3</sub> at 110-140° see (3) (2); for prepn. (67% yield (1)) from 2,4-dichlorobenzohydrol by oxidn. with CrO<sub>2</sub> in AcOH see (1) }

C fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (1) *m*-dichlorobenzene (3:5960) and BzOH (1.0715) (92% yield (1)).

[C does not give a smooth reaction with NaOMe (2) ]

3:0825 (1) Lock, Rödiger, *Ber.* 72, 868-869 (1939). (2) van de Lande, *Rec. trav. chim.* 51, 99, 105 (1932). (3) Böseken, *Rec. trav. chim.* 27, 15 (1908).

3:0840 2,7-DICHLORO-2,7-DIMETHYLOCTANE



Beil. I —  
I<sub>1</sub>— (60)  
I<sub>2</sub>—

M.P. 40° (1)



3: 8777  $\gamma$ -PHENYL-*n*-PROPYL CHLORIDE $C_9H_{11}Cl$ 

Beil. V - 391.

( $\gamma$ -Chloro-*n*-propylbenzene,  
hydrocinnamyl chloride)V<sub>1</sub>-(190)V<sub>2</sub>-(305)

B.P. 219-220° cor. (1) (3) (13)

 $D_4^{25} = 1.056$  (7)  $n_D^{25} = 1.52030$  (2)

106-106.5° at 22 mm. (2)

1.5160 (6)

110° at 21 mm. (3) (13)

 $D_{25}^{25} = 1.04259$  (2)

95-97° at 12 mm. (10)

93.5-95° at 11 mm. (4)

 $D_{25}^{25} = 1.0801$  (6)

85-87° at 9 mm. (5)

89-93° at 6 mm. (6)

[For prepn. of  $\bar{C}$  from  $\gamma$ -phenyl-*n*-propyl alc. (hydrocinnamyl alc.) (1:6520) with fung. HCl in s.t. at 130° (1) (15) or 140-150° (3), or in s.t. at 100° for 8 hrs. (77% yield (5)), or with  $ZnCl_2$  + conc. HCl (40% yield (8)) (2) see indic. refs.; with  $SOCl_2$  in ether (82% yield (9)) or pyridine (48.5% yield (10)) or dimethylaniline (70.5% yield (10)) see indic. refs. (for intermediate formn. of  $\gamma$ -phenyl-*n*-propyl chlorosulfite and bis-( $\gamma$ -phenyl-*n*-propyl) sulfite in this reactn. see (11)); from  $\gamma$ -chloro-*n*-propyl *p*-toluenesulfonate (2 moles) with  $C_6H_5MgBr$  in ether (yield: 62% (6), 31% (12)) see indic. refs.; from  $C_6H_5CH_2MgCl$  with di-( $\beta$ -chloroethyl) sulfate in ether (66% yield) see (4); from  $\alpha$ -( $\gamma$ -chloro-*n*-propyl)-aniline via diazotization and treatment with alk. +  $SnCl_2$  (75% yield (3)) (13) see indic. refs.; from *N*-methyl-*n*-( $\gamma$ -phenyl-*n*-propyl)benzamide with  $PCl_5$  see (14).]

$\bar{C}$  is not decomposed on boilg. with  $ZnCl_2$  and does not react at 100° with  $AgOAc$  (1).

[ $\bar{C}$  boiled for 8 hrs. with excess 5%  $NaOMe$  in  $MeOH$  gives (86% yield (15))  $\gamma$ -phenyl-*n*-propyl methyl ether [Beil. VI<sub>1</sub>-(252)], b.p. 206.5° at 758.5 mm. u.c., h.p. 100-102° at 20 mm. (15);  $\bar{C}$  with  $KOH$  in  $EtOH$  refluxed 2 hrs. gives (1)  $\gamma$ -phenyl-*n*-propyl ethyl ether [Beil. VI-503], h.p. 224° cor.;  $\bar{C}$  boiled several hours with excess conc. alc.  $NaOC_2H_5$  gives (100% yield (3))  $\gamma$ -phenyl-*n*-propyl phenyl ether [Beil. VI-504, VI<sub>1</sub>-252], h.p. 182-183° at 17 mm. (3).]

[ $\bar{C}$  on boilg. several hours with alc.  $NaI$  yields (3)  $\gamma$ -phenyl-*n*-propyl iodide, h.p. 137-140° at 20 mm. (3) (for rate of reactn. of  $\bar{C}$  with  $KI$  in acetone at 50° see (5)).]

[ $\bar{C}$  with activated  $Mg$  in dry ether gives (98% yield (9))  $C_6H_5CH_2CH_2CH_2MgCl$ ; for reactn. of this  $RMgCl$  cpd. with various carbonyl cpds., e.g., acrolein (10), ethyl phenyl ketone (9), or cyclopentanone (16), see indic. refs.]

[ $\bar{C}$  with  $AlCl_3$  in  $CS_2$  or lgr. gives (17) about 10% hydrindene (1:7511), b.p. 177°, together with other products.]

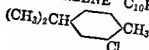
[ $\bar{C}$  on mononitration with 4 vols.  $HNO_3$  ( $D = 1.5$ ) below -10° gives over 90% yield (18) of  $\gamma$ -(*p*-nitrophenyl)-*n*-propyl chloride [Beil. V<sub>1</sub>-191], h.p. 176-180° at 15 mm. with sl. dec. (18).]

3: 8777 (1) Errera, *Gazz. chim. ital.* 16, 313-314 (1886). (2) Goebel, Wenzke, *J. Am. Chem. Soc.* 60, 698 (1938). (3) von Braun, *Ber.* 43, 2841-2842 (1910). (4) Suter, Evans, *J. Am. Chem. Soc.* 60, 536-537 (1938). (5) Conant, Kirner, *J. Am. Chem. Soc.* 46, 242, 249 (1924). (6) Rossander, Marvel, *J. Am. Chem. Soc.* 50, 1495 (1928). (7) Dunstan, Hilditch, Thole, *J. Chem. Soc.* 103, 140 (1913). (8) Norris, Taylor, *J. Am. Chem. Soc.* 46, 756 (1924). (9) Gilman, Harris, *J. Am. Chem. Soc.* 54, 2075 (1932). (10) Cohen, *J. Chem. Soc.* 1935, 433.

(11) Carré, Libermann, *Compt. rend.* 198, 274-276 (1934). (12) Gilman, Beaber, *J. Am. Chem. Soc.* 45, 842 (1923). (13) Merck, *Ger.* 239,076, Oct. 9, 1911; *Cent.* 1911, II 1393. (14) von Braun, *Aust. Ber.* 49, 507 (1916). (15) Straus, Berkow, *Ann.* 401, 151 (1913). (16) Denis-senko, *Ber.* 69, 2186 (1936). (17) von Braun, *Deutsch. Ber.* 45, 1269 (1912).

LIQUIDS WITH  $D_4^{20} < 1.15$ 3:8775 2-CHLORO-4-ISOPROPYL-1-METHYLBENZENE  
(2-Chloro-*p*-cymene)

3:8775

C<sub>10</sub>H<sub>13</sub>Cl Beil. V - 423  
V<sub>1</sub>—  
V<sub>2</sub>-(325)

B.P. 217.6°		
216-218°	at 760 mm.	(1)
216-218°	at 762 mm.	(2) (3)
216-217°	cor. at 746 mm.	(4)
215-218°	at 761 mm.	(5)
214-216°		(6)
213-216°		(7)
213-214°		(8)
117°	at 764 mm.	(9)
103-105°	at 35 mm.	(4)
85-90°	at 19 mm.	(10)
	at 5 mm.	(6)

 $D_4^{17} = 1.0208$  (5)  
 $1.0152$  (?) (2)
 $n_D^{17} = 1.51776$  (5) (2)

[For prepn. of  $\bar{C}$  from carvacrol (2-hydroxy-*p*-cymene) (1·1760) with  $\text{PCl}_5$  see (1) (11); refs.; from 2-amino-*p*-cymene (cyanidine) (carvacrylamine) [Beil. XII-1171, XII-1-(506)] via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reactn see (2) (9); from carvone (1·5540) (13) or eucarvone [Beil. VII-151, VII-(99)] (13) or carvenone [Beil. VII-78, VII-(66)] (10) with  $\text{PCl}_5$  (cf. (14) (15)) see indic. refs.]

$\bar{C}$  on oxidn. with boilg. dil.  $\text{HNO}_3$  yields (12) (8) (11) (10) 3-chloro-4-methylbenzoic acid (3-chloro-*p*-toluic acid) (3·4900), m.p. 199° (10), 196° (8), 194-195° (12).

$\bar{C}$  on dinitration with 10-12 pts  $\text{HNO}_3$  ( $D = 1.5$ ) below 0° (2) (16) (18) or with a mixt. of conc. or fumg.  $\text{HNO}_3$  + fumg.  $\text{H}_2\text{SO}_4$  as directed (2) (8) (6) yields 5,6-dinitro-2-chloro-*p*-cymene, cryst. from  $\text{AcOH}$  (2), dil.  $\text{AcOH}$  (2),  $\text{EtOH}$  (6), or dil.  $\text{MeOH}$  (16), m.p. 111.0-111.5° cor (18), 109.5-110.5° (2), 109.5° (8), 108-109° (6) [This prod. refluxed with 5-10 pts. piperidine for 20-60 min at 100° gives 3,5-dinitro-2-piperidino-*p*-cymene, yel. ndls. from  $\text{AcOH}$  (2) or from dil. alc. (18) (16), m.p. 123-124° (16), 122.5-123.5° (18), 122-123° (2).] [Note that the original structure assigned by (6) to dinitro- $\bar{C}$  has been confirmed by (18) despite intermediate contrary views (2) (16).]

[ $\bar{C}$  with  $\text{Br}_2$  + Fe at ord. temp. yields (17) 5-bromo-2-chloro-*p*-cymene, b.p. 247° (17).]

3:8775 (1) Kobe, Okabe, Ramstad, Huemmer, *J. Am. Chem. Soc.* 63, 3251-3252 (1941) (2) Ganguly, R. J. W. LeFevre, *J. Chem. Soc.* 1934, 852-854. (3) Ganguly, R. J. W. LeFevre, *J. Chem. Soc.* 1934, 1699 (4) Fileti, Crosa, *Gazz. chim. ital.* 18, 299 (1858). (5) C. G. LeFevre, R. J. W. LeFevre, K. W. Robertson, *J. Chem. Soc.* 1935, 480-488. (6) Lubs, Young, *J. Ind. Eng. Chem.* 11, 1130-1133 (1919). (7) Junger, Klages, *Ber.* 29, 315 (1896). (8) Hintikka, *Ann. Acad. Sci. Fennicae* 19-A, No. 10, 6 pp. (1923). *C.A.* 19, 42 (1925). (9) R. J. W. LeFevre, *J. Chem. Soc.* 1933, 980-984 (10) Marsh, Hartridge, *J. Chem. Soc.* 73, 854-855 (1898). (11) Fleischer, Kehulé, *Ber.* 6, 1090 (1873). (12) Vongerichten, *Ber.* 10, 1249-1252 (1877). (13) Klages, Kraith, *Ber.* 32, 2554, 2558, 2560 (1899). (14) Semmler, *Ber.* 41, 4478 (1908). (15) Wallach, *Ann.* 368, 15 (1909). (16) R. J. W. LeFevre, *J. Chem. Soc.* 1933, 980. (17) Varma, Srinivasan, *J. Indian Chem. Soc.* 13, 190-191 (1936). (18) Qvist, Kajander, *Acta Acad. Aboensis, Math. et Phys.* 13, No. 10, 16 pp. (1942); *Cent.* 1942, II 26-28; *C.A.* 37, 4370-4372 (1943).

*p*-CHLOROPHENOLC<sub>6</sub>H<sub>5</sub>OClBeil. VI - 186  
VI<sub>1</sub>-(100)  
VI<sub>2</sub>-(174)B.P. 218-219°  
M.P. 42-43°  
See 3:0475 Division A: Solids.

3:8783 *d,l*- $\alpha$ -CHLORO-*n*-VALERIC ACID

Beil. II-302

 $\Pi_1-$  $\Pi_2-$ 

B.P.

F.P.

222° at 763 mm. (1)    -15° (1)     $D_{\text{D}}^{13.2} \approx 1.141$  (1)     $n_{\text{D}}^{11} = 1.44807$  (1)  
 132-135° at 32 mm. (1)

Oil; insol. aq., sol. in alc., ether.

[For prepn. of  $\bar{C}$  from  $\alpha$ -chloro-*n*-valeronitrile by hydrolysis with conc. HCl see (1) (2).]  
 [The levorotatory isomer of  $\bar{C}$ , b.p. 80-84° at 1 mm., has been obtd. (3) from dextrorotatory 3-chlorohexene-1 by ozonolysis in  $\text{CHCl}_3$ , decompn. with aq., and  $\text{Br}_2/\text{aq.}$  oxidn. of the resultant aldehyde.]

—  $\alpha$ -Chloro-*n*-valeramide: cryst. from alc. + aq. (3:1), m.p. 70-70.2° (4). [Prepd. indirectly from  $\alpha$ -chloro-*n*-valeronitrile with conc. HCl (4).]

—  $\alpha$ -Chloro-*n*-valer-anilide: unreported.

—  $\alpha$ -Chloro-*n*-valero-*p*-toluidide: unreported.

3:8783 (1) Servais, *Rec. trav. chim.* 20, 45-46 (1901). (2) Henry, *Bull. acad. roy. Belg.* (3) 36, 241-262 (1898); *Cent.* 1898, I 194. (3) Levene, Haller, *J. Biol. Chem.* 83, 596 (1929). (4) Vandewijer, *Bull. soc. chim. Belg.* 45, 255 (1936).

## — 4-CHLORO-2-METHYLPHENOL



Beil. VI-(359)

VI<sub>1</sub>-(174)VI<sub>2</sub>-(332)

B.P. 220-225°

M.P. 48-49°

See 3:0780. Division A: Solids.

3:8784 6-CHLORO-2,4-DIMETHYLPHENOL  
(5-Chloro-*m*-4-xylene)

Beil. VI-489

VI<sub>1</sub>-(241)VI<sub>2</sub>—

B.P. 221-223° at 760 mm. (1)

100-101° at 17 mm. (2)

100-101° at 16 mm. (3)

86.5-87° at 9 mm. (2)

Oil with phenolic odor. — Sol. aq., eas. sol. org. solvents. — Volatile with steam.

[For prepn. of  $\bar{C}$  from 2,4-dimethylphenol (*unsym.*-*m*-xylene) (1:1740) by chlornation with acet-*N*-chloro-2,4-dichloroanilide in AcOH contg. HCl at 15° as directed (1), or with  $\text{SO}_2\text{Cl}_2$  in AcOH (3), see indic. refs.; from 6-amino-2,4-dimethylphenol hydrochloride [Beil. XIII-630, XIII<sub>1</sub>-(245)] via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reaction (77% yield) see (2); for formn. of  $\bar{C}$  from 2,4-dimethylquinol (*m*-xyloquinol) [Beil. VIII-22, VIII<sub>1</sub>-(514)] by action of HCl (some of the isomeric 5-chloro-2,4-dimethylphenol (3:2460) also being formed) see (2) (4).]

—  $\beta$ -PHENOXYETHYL CHLORIDE

$C_8H_9OCl$

Beil. VI - 142



VI<sub>1</sub>—

VI<sub>2</sub>-(144)

B.P. 220°

M.P. 28°

See 3:0165. Division A: Solids.

3:8780 NEOPHYL CHLORIDE (1)  
( $\beta$ -Chloro-*ter*-butyl)benzene;  
( $\beta$ -chloro- $\alpha,\alpha$ -dimethyl)ethylbenzene

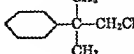
$C_{10}H_{13}Cl$

Beil. V —

CH<sub>3</sub>

VI—

VI<sub>2</sub>-(320)



B.P. 221° dec. at 741 mm. (1)

$n_D^{20} = 1.5250$  (1)

111° at 90 mm. (2)

1.5253 (3)

110-120° at 30 mm. (3)

1.5248 (8)

104-105° at 20 mm. (5)

104-105° at 18 mm. (4)

97° at 13 mm. (1)

95° at 10 mm. (1)

53° at 1 mm. (8)

[For prepn. of  $\bar{C}$  from benzene (1:7400) + methallyl chloride (3-chloro-2-methylpropene-1) (3:7145) by condensation in presence of conc.  $H_2SO_4$  (68% yield (1)) or HF (66% yield (2)) see (1) (2); for formn. from *ter*-butylbenzene (1:7460) by treatment with  $SO_2Cl_2$  see (3); for formn. from corresp. alc. (2-methyl-2-phenylpropanol-1) with  $SOCl_2$  see (5) (4).]

$\bar{C}$  btd. with 13% alc. KOH at 86° for 24 hrs. is unchanged (2);  $\bar{C}$  refluxed 11½ hrs. with NaOEt in abs. alc. (1) or refluxed 9½ hrs. with pyridine (1) is recoverable to extent of 87-88% (1).

[For study of behavior of  $\bar{C}$  with Na, Na in liq.  $NH_3$ , NaEt,  $NaNH_2$ , etc., or on pyrolysis see (1).]

$\bar{C}$  with sublimed Mg (not comml. Mg even after activation) + a trace of  $I_2$  yields (3) neophyl  $MgCl$ ; this  $RMgCl$  on oxidation with  $O_2$  gives (71.6% yield (1)) the corresp. alc., 2-methyl-2-phenylpropanol-1, b.p. 131° at 30 mm. (1), 122-123° at 20 mm. (5),  $n_D^{20} = 1.5261$  (*N*-phenylcarbamate, m.p. 59-60° (5), 59.5-60.5° (1); *N*-( $\alpha$ -naphthyl)carbamate, m.p. 01.5-02.5° (1)). [For behavior of  $\bar{C}$  with  $C_6H_5MgBr$  in pres. of  $CoBr_2$  see (8).]

③  $\beta$ -Phenylisovaleric acid: cryst. from pet. eth., m.p. 57.5-58.5° (6), 58-59.5° (1).

[From  $RMgCl$  on carbonation and subsequent hydrolysis, yield 81.6% (1).]

④  $\beta$ -Phenylisovaleranilide: m.p. 122-123° (3), 121-123° (6) [from  $RMgCl$  by reactn. with phenyl isocyanate (3)].

⑤ *p*-Acetamino-( $\beta$ -chloro-*ter*-butyl)benzene: m.p. 155-156° (7). [From  $\bar{C}$  by nitration, reduction, and acetylation (7).]

3:8780 (1) Whitmore, Weisgerber, Shablen, *J. Am. Chem. Soc.* **63**, 1469-1471 (1943). (2) Calcott, Tinker, Weinmayr, *J. Am. Chem. Soc.* **61**, 1012 (1939). (3) Calcott, Tinker, Weinmayr, *J. Am. Chem. Soc.* **61**, 2147-2148 (1939). (4) Haller, Ramart, *Chim. Ind. (Milan)* **39**, 10-14 (1915). (5) Haller, Bauer, *Ann. chim. (5)* **9**, 10-14 (1915). (6) Ipatieff, Schwerling, *J. Am. Chem. Soc.* **67**, 1438-1440 (1945). (7) Ipatieff, Schwerling, *J. Am. Chem. Soc.* **67**, 1438-1440 (1945).

## — 3-CHLORO-4-METHYLPHENOL

 $C_7H_7OCl$ 

Beil. VI-402

VI<sub>1</sub>—VI<sub>2</sub>—

B.P. 228° at 760 mm.

M.P. 55°

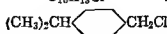
See 3:1025. Division A: Solids.

## 3:8795 4-ISOPROPYLBENZYL CHLORIDE

(Cumyl chloride; 1-chloromethyl-4-isopropylbenzene)

 $C_{10}H_{13}Cl$ 

Beil. V-423

V<sub>1</sub>—V<sub>2</sub>-(326)

B.P.

F.P.

228° with part. dec. (1)

-29° (8)

 $D_4^{21.5} = 1.020$  (1) $n_D^{21.5} = 1.523$  (1)

227-228° (2)

226-229° (3)

225-229° (4)

116-118° at 22 mm. (5)

110° cor. at 15 mm. (1)

108-109° at 14 mm. (6)

100° at 14 mm. (7)

Liq. with odor and lachrymatory effect less than that of benzyl chloride (3:8535) but with irritating effect on skin (1). —  $\bar{C}$  on boilg. (4) (espec. in presence of  $ZnCl_2$ ) partially dec. with formn. of a hydrocarbon  $C_{20}H_{24}$  (probably 2,6-di-isopropyl-9,10-dihydroanthracene [Beil. V-654]), yel. pdr., m.p. 90° (4).

[For prepn. of  $\bar{C}$  from *p*-isopropylbenzene (cumene) (1:7440) with trioxymethylene (75% yield (1)) or formalin (75% yield (7)) +  $HCl$  +  $ZnCl_2$  see (1) (7); with chloromethyl methyl ether (3:7085) +  $SnCl_4$  see (8); from *p*-cymene (1:7505) by direct chlorination see (4) (3) (9); from cumylal alc. [Beil. VI-543] with dry  $HCl$  (10) or const.-boilg.  $HCl$  (100% yield (2)) see (10) (2) (9).]

$\bar{C}$  with  $Zn$  +  $HCl$  reduces (10) to *p*-cymene (1:7507). —  $\bar{C}$  on boilg. with aq.  $Pb(NO_3)_2$  soln. (7) or alk.  $Na_2Cr_2O_7$  (12) yields *p*-isopropylbenzaldehyde (cuminaldehyde) (1:0234). —  $\bar{C}$  with aq. alk. presumably (no record) yields cumyl alcohol [Beil. VI-543] but with alc.  $KOH$  gives (4) ethyl cumyl ether [Beil. VI-544], b.p. 227° (4).

$\bar{C}$  with  $Mg$  in dry ether yields (9) cumyl  $MgCl$  accompanied by some hicumyl (4,4'-diisopropylidihenzyl) [Beil. V-623], m.p. 58° (9); the  $R.MgCl$  with aq. gives (74% yield (1)) *p*-cymene (1:7505); the  $R.MgCl$  upon treatment with  $O_2$  gas gives (71-80% yield (9)) cumyl alcohol [Beil. VI-543], b.p. 246° cor. (9), 140° at 20 mm. (9); the  $R.MgCl$  with  $CO_2$  gives (73% yield (9)) after acidification *p*-isopropylphenylacetic acid (homocuminic ac.) [Beil. IX-561], m.p. 52°, b.p. 195° at 30 mm., 190° at 25 mm.,  $D_4^{15} = 1.039$ ,  $n_D^{15} = 1.522$  (9). [The  $R.COOMgCl$  cpd. if treated with isopropyl  $MgCl$  gives mainly (11) *p*-isopropylmalonic ac., m.p. 143.5° dec. (1).]

3:8795 (1) Bert, *Bull. soc. chim.* (4) 37, 1266-1268 (1925). (2) Norris, Mulliken, *J. Am. Chem. Soc.* 42, 2098 (1920). (3) Varma, Srinivasan, *J. Indian Chem. Soc.* 13, 191 (1936). (4) Errera, *Gazz. chim. ital.* 14, 277-283 (1884). (5) Jones, *J. Chem. Soc.* 1938, 1416. (6) Baker, Nathan, *J. Chem. Soc.* 1935, 1844. (7) Blanc, *Bull. soc. chim.* (4) 33, 317 (1923). (8) Darzens, Levy, *Compt. rend.* 194, 2057 (1932). (9) Bert, *Bull. soc. chim.* (4) 37, 1577-1583 (1925). (10) Paterno, Spica, *Gazz. chim. ital.* 9, 397-398 (1879).

(11) Ivanoff, Pehénitchny, *Bull. soc. chim.* (5) 1, 229 (1934). (12) Blanc, *Ger.* 347,583, Jan. 23, 1922; *Cent.* 1922, II 1138.

[For studies of haetericidal action of  $\tilde{C}$  see (3) (5).]

The nitration of  $\tilde{C}$  has not been reported, and none of its mononitro- or dinitro-derivs. are known; for patent on sulfonation of  $\tilde{C}$  see (6).

$\tilde{C}$  in alc. soln. with  $FeCl_3$  gives olive-green color turning brown on htg.

— 6-Chloro-2,4-dimethylphenyl acetate: unreported.

— 6-Chloro-2,4-dimethylphenyl benzoate: oil (2).

⑥ 6-Chloro-2,4-dimethylphenyl *p*-nitrobenzoate: m.p. 94-94.5° (2). [From  $\tilde{C}$  + *p*-nitrobenzoyl chloride in pyridine (2)]

⑦ 6-Chloro-2,4-dimethylphenyl *N*-phenylcarbamate: m.p. 129-130° (2). [From  $\tilde{C}$  + phenyl isocyanate at 150-200° (2).]

3:8784 (1) Orton, King, *J. Chem. Soc.* 99, 1191 (1911). (2) Bamberger, Reber, *Ber.* 46, 793-795, 799-799 (1913). (3) Heicken, *Angew. Chem.* 52, 263-265 (1939). (4) Bamberger, Reber, *Ber.* 40, 2268 (1907). (5) Lockemana, Kunzmann, *Angew. Chem.* 46, 296-301 (1933). (6) Weiler, Better (to I.G.), Ger. 557,450, Aug. 21, 1931; *Cent.* 1932, II 2370-2371; [*C.A.* 27, 735 (1938)].

3:8785 1-CHLORODECANE  $CH_3(CH_2)_9CH_2Cl$   $C_{10}H_{21}Cl$  Beil. I - 169  
 (n-Decyl chloride)  $I_1$ —  
 $I_2$ -(129)

B.P. 223.0-223.5°	at 760 mm. (1)	$D_4^{25} = 0.8850$ (4)	$n_D^{25} = 1.4400$ (4)
223-223°	at 760 mm. (7)	$D_4^{20} = 0.8696$ (1)	$n_D^{20} = 1.43799$ (1)
180-190°	at 720 mm. (2)	0.8683 (7)	1.43731 (7)
130-140°	at 80 mm. (3)	$D_4^{20.5} = 0.8621$ (6)	$n_D^{20.5} = 1.4368$ (6)
122°	at 50 mm. (2)		
137-142°	at 24 mm. (4)		
100.8-101.0°	at 12 mm. (5)		
106°	at 16 mm. (6)		

Colorless oil with characteristic odor (1).

[For prepn. of  $\tilde{C}$  from decanol-1 (1:6275) with  $PCl_5$  in  $CCl_4$  see (1); with  $SOCl_2$  + pyridine (80% yield (5)) or  $SOCl_2$  without pyridine (91% yield (7)) see (5) (7); for prepn. from *n*-heptyl  $MgBr$  +  $\gamma$ -chloro-*n*-propyl *p*-toluenesulfonate see (4).]

$\tilde{C}$  htd. at 100° with aq.  $Ba(OH)_2$  yields (2) decanol-1 (1:6275).

$\tilde{C}$  with  $Mg$  in dry ether contg. trace of  $I_2$  gives (96% yield in 9 hrs. (8))  $RMgCl$ .

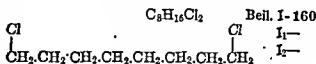
(2) Schultz, *Ber.* 42, 3610-3611  
 nder, Marvel, *J. Am. Chem. Soc.*  
 69 (1933). (6) Rothstein, *Bull.*  
 11, 338, 641. (8) Houben, Boedler,

[For prepn. (80% yield (1)) from undecanol-1 (1:5890) +  $\text{SOCl}_2$  + pyridine see (1), or with  $\text{SOCl}_2$  alone (89% yield) see (2).]

No other data on  $\bar{C}$  are recorded.

3:8803 (1) Rothstein, *Bull. soc. chim.* (5) 2, 84 (1935). (2) Vogel, *J. Chem. Soc.* 1943, 638, 641.

3:8805 1,8-DICHLORO-OCTANE  
(Octamethylene dichloride)



B.P. 240-242° (1)

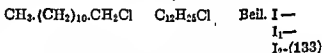
[For formn. of  $\bar{C}$  from octamethylenediamine [Beil. IV-271] with  $\text{NOCl}$  see (1); from 1,8-diphenoxyoctane (see below) with fuming  $\text{HCl}$  see (1).]

$\bar{C}$  htd. with sodium phenolate yields (1) (2) 1,8-diphenoxyoctane [Beil. VI-148; VI-1-(85)], colorless ths., m.p. 83.5-84°, sol. in hot alc., in ether, or in  $\text{C}_6\text{H}_6$ ; not volatile with steam. [This prod. splits with  $\text{HCl}$  to yield (1)  $\bar{C}$ ; with  $\text{HBr}$  to yield (1) 1,8-dibromooctane [Beil. I-160], m.p. 15-16°, h.p. 270-272° sl. dec., h.p. 150-161° at 20-25 mm. (1).]

$\bar{C}$  refluxed with  $\text{NaI}$  in acetone for 4 hrs., solvent evaporated, ether-sol. portion of residual oil htd. for 4 hrs., with thiourea in isoamyl alc. gives (3) octamethylene bis-( $\omega, \omega'$ -isothiourca hydrochloride), m.p. 185-186° (3).

3:8805 (1) Ssolonina, *J. Russ. Phys.-Chem. Soc.* 30, 620, 623 (1898); *Cent.* 1899, I 26. (2) Ssolonina, *J. Russ. Phys.-Chem. Soc.* 30, 822, 824 (1898); *Cent.* 1899, I 254. (3) Kawai, Hosono, Shikunami, Yonechi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* 16, Nos. 306-309, 9-10 (1931); *Cent.* 1931, II 1694; *C.A.* 25, 5665 (1931).

3:8810 1-CHLORODODECANE  
(*n*-Dodecyl chloride;  
*n*-lauryl chloride)



B.P. 243-244° cor. (1)	$D_4^{22} = 0.8673$ (3)	$n_D^{22} = 1.4421$ (3)
132-134° at 18 mm. (2)	$D_4^{20} = 0.8673$ (9)	$n_D^{20} = 1.44255$ (9)
130° at 15 mm. (3)		
125-126° at 10 mm. (4)		
116.5° at 5 mm. (9)		

[For prepn. (80% yield (3)) from dodecanol-1 (1:5900) +  $\text{SOCl}_2$  + pyridine see (3); or with  $\text{SOCl}_2$  in absence of pyridine (84% yield) see (9).]

$\bar{C}$  in alc. refluxed with thiourea for 4 days gives (5) *S*-*n*-dodecylisothiourca hydrochloride, m.p. 132-135° (5).

[For reactn. of  $\bar{C}$  with liq.  $\text{NH}_3$  see (6) (7); with various amines see (7) ]

[For reactn. of  $\bar{C}$  with  $\text{KI}$  see (1); for reactn. with  $\text{Mg}$  + ether see (2); for reaction of  $\bar{C}$  with  $\text{Li}$ ,  $\text{Na}$ , or  $\text{K}$  followed by  $\text{CO}_2$  see (10).]

$\bar{C}$  htd. with pyridine in s.t. at 110° for 15 hrs. yields (8) *n*-dodecylpyridinium chloride, cryst. from alc. + ether or from  $\text{C}_6\text{H}_6$  as monohydrate, m.p. 92° (8). [This quat. salt yields (8) on cat. hydrogenation *N*-(*n*-dodecyl)piperidinium hydrochloride, m.p. 188-189° (8).]

—*n*-Dodecyl mercuric chloride ( $\text{C}_{12}\text{H}_{25}\text{HgCl}$ ): m.p. 114.0-114.5° (10). [Prepd. indirectly (10).]

3:8810 (1) Conant, Hussey, *J. Am. Chem. Soc.* 47, 485 (1925). (2) Oldham, Ubbelohde, *J. Chem. Soc.* 1938, 204. (3) Rothstein, *Bull. soc. chim.* (5) 2, 84 (1935). (4) Reed, Tartar, *J. Am.*

3:8800 *n*-DECANOYL CHLORIDE  $\text{CH}_3(\text{CH}_2)_8\text{C}(=\text{O})\text{Cl}$   $\text{C}_{10}\text{H}_{19}\text{OCl}$  Beil. II-356  
(*n*-Caprinyll chloride)  $\text{Cl}$  II<sub>1</sub>—  
II<sub>2</sub>—

B.P. 232.3° at 760 mm. (1) F.P. -34.5° (1)  
120° at 20 mm. (2)  
114° at 15 mm. (3)  
111-112° at 14 mm. (4)  
104-105° at 9 mm. (5)  
105-107° at 8-9 mm. (6)

Care must be taken not to confuse  $\bar{\text{C}}$ , the acid chloride of *n*-capric acid, with the corresponding relatives of *n*-caprylic acid ( $\text{C}_8$ ) and of *n*-caproic acid ( $\text{C}_6$ ); for this reason the name *n*-decanoyl chloride is preferred.

[For prepn. of  $\bar{\text{C}}$  from *n*-decanoic acid (*n*-decylic acid) (*n*-capric acid) (1:0585) with  $\text{PCl}_5$  (3), with  $\text{PCl}_3$  (70% yield (1)), with  $\text{POCl}_3$  (7), with oxalyl (di)chloride (3:5060) (5), or with  $\text{SOCl}_2$  (6) (94% yield (4)) see indic. refs.]


[For use of  $\bar{\text{C}}$  in prepn. of corresp. cellulose esters see (8) (9); for use in syntheses of various glycerides see (5) (6); for use in prepn. of derivs. of vanillylamine see (2) (10), for cat. hydrogenation to *n*-decylaldehyde (1:0222) see (11).]

$\bar{\text{C}}$  on hydrolysis (or even slowly in moist air) yields *n*-decanoic acid (1:0585) q.v. (for the amide, amide, *p*-toluidide, and other derivatives corresponding to  $\bar{\text{C}}$  see 1:0585).

3:8800 (1) Deffett, *Bull. soc. chim. Belg* 40, 389-391 (1931). (2) Ford-Moore, Phillips, *Rec. trav. chim.* 53, 856 (1934). (3) Krafft, Koenig, *Ber* 23, 2385 (1890). (4) Fierz-David, Kuster, *Helv. Chim. Acta* 22, 86-89 (1939). (5) Averill, Roche, King, *J. Am. Chem. Soc.* 51, 868 (1929). (6) Deffett, *Bull. soc. chim. Belg* 40, 389-391 (1931). (7) Grimm, *Ann* 157, 272-273, IV 961. (8) Brit. 313,616, Aug 8, 1923. (9) Soc. 42, 2125 (1919). (10) 139.

— PHENYL CHLOROACETATE  $\text{C}_6\text{H}_5\text{O}_2\text{Cl}$  Beil. VI - 153  
 $\text{Cl} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_5$  VI<sub>1</sub>-(87)  
VI<sub>2</sub>-(154)  
B.P. 230-235° M.P. 45°  $D_4^{44} = 1.2202$   $n_D^{44} = 1.5146$

See 3:0565 Division A: Solids.

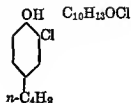
— 4-CHLORO-3-METHYLPHENOL  $\text{C}_7\text{H}_7\text{OCl}$  Beil. VI - 381  
 VI<sub>1</sub>-(187)  
VI<sub>2</sub>-(355)  
B.P. 235° M.P. 57°

See 3:1535. Division A: Solids.

3:8803 1-CHLOROUNDECANE  $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{Cl}$   $\text{C}_{11}\text{H}_{23}\text{Cl}$  Beil. S.N. 10  
(*n*-Undecyl chloride;  
1-chlorohendecane)

B.P. 240-241° at 772 mm. (2)  $D_4^{21.5} = 0.8570$  (1)  $n_D^{21.5} = 1.4350$  (1)  
117° at 16 mm. (1)  $D_4^{20} = 0.8677$  (2)  $n_D^{20} = 1.44003$  (2)



3:8830 2-CHLORO-4-*n*-BUTYLPHENOL

Beil. S.N. 530-a

B.P. 247-248° at 760 mm. (1) (4)

243-244° at 735 mm. (2)

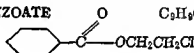
110-115° at 3 mm. (3) (4)

[For prepn. of  $\bar{\text{C}}$  from *p*-*n*-butylphenol (1:1771) by chlorination with  $\text{Cl}_2$  (3),  $\text{SO}_2\text{Cl}_2$  (4) (5); or  $\text{ClSO}_3\text{H}$  (5) see indic. refs.; for prepn. of  $\bar{\text{C}}$  from *o*-chlorophenyl propionate by rearr. with  $\text{AlCl}_3$  in nitrobenzene to *n*-propyl 3-chloro-4-hydroxyphenyl ketone and subsequent reductn. to  $\bar{\text{C}}$  see (4) (1).]

[For studies of bactericidal characteristics of  $\bar{\text{C}}$  see (1) (2) (6).]

$\bar{\text{C}}$  with  $\alpha$ -naphthoyl chloride (3:6930) yields (2) 4-*n*-butyl-2-chlorophenyl  $\alpha$ -naphthoate, m.p. 44-46° (2).

3:8830 (1) Klarmann, Shternov, Gates, *J. Am. Chem. Soc.* 55, 2576-2589 (1933). (2) Blicke, Stockhaus, *J. Am. Pharm. Assoc.* 22, 1090-1092 (1933); *Cent.* 1934, I 1642; *C.A.* 28, 4839 (1934). (3) Klarmann (to Lehn & Fink Products Corp.), U.S. 2,010,505, Aug. 6, 1935; *Cent.* 1936, I 810; *C.A.* 29, 6608 (1935). (4) Klarmann (to Lehn & Fink Products Corp.), U.S. 2,139,550, Dec. 6, 1938; *Cent.* 1939, I 1807; *C.A.* 33, 2285 (1939). (5) Blicke (to Regents of Univ. of Michigan), U.S. 1,980,966, Nov. 13, 1934; *Cent.* 1935, I 3312; *C.A.* 29, 476 (1935). (6) Klarmann, Shternov, Gates, *J. Lab. Clin. Med.* 20, 40-47 (1934).

3:8860  $\beta$ -CHLOROETHYL BENZOATE

Beil. IX-112

IX<sub>1</sub>-

B.P. 255-257° at 762 mm. (1)

256-257° at 762 mm. (2)

254-255° at 749 mm. (3)

138.8° at 18 mm. (1)

125-130° at 14 mm. (4)

120-122° at 5 mm. (5)

118-120° at 2 mm. (6)

Oil, insol. aq.; eas. sol. alc., ether.

[For prepn. of  $\bar{\text{C}}$  from ethylene chlorohydrin (3:5552) with  $\text{BzCl}$  (3:6240) on htg. (yields: 90% (1), 84.5% (6), 55% (2)) (5) see indic. refs.; from ethylene glycol (1:6465) with benzoic acid (1:0715) at 100° in pres. of  $\text{HCl}$  gas (7); from ethylene oxide (1:6105) with  $\text{BzCl}$  (3:6240) at 190° (8); from 1,4-dioxane (1:6400) with  $\text{BzCl}$  (3:6240) +  $\text{TiCl}_4$  (2 moles) at 150-180° for 10 hrs. (70% yield (9)); from ethylene +  $\text{BzOH}$  (1:0715) +  $\text{Cl}_2$  + cat. as directed (10) see indic. refs.]


[For formn. of  $\bar{\text{C}}$  from  $\beta$ -chloroethyl iminobenzoate on warming (3), from  $\beta$ -chloroethyl *p*-toluenesulfonate with  $\text{C}_6\text{H}_5\text{COOMgBr}$  (5% yield (11)), or from *bis*-( $\beta$ -chloroethyl) sulfate with  $\text{NaOBz}$  at 170° (61.5% yield (4)) see indic. refs.]

$\bar{\text{C}}$  on htg. either alone or with  $\text{SnCl}_4$  at 180-200° for 25 hrs. gives (9) ethylene glycol dibenzoate, m.p. 73°.

[ $\bar{\text{C}}$  on a mononitration is claimed (1) to yield mainly  $\beta$ -chloroethyl *m*-nitrobenzoate, but this alleged prod. is not described either in the article or elsewhere in the literature.]

$\bar{\text{C}}$  with  $\text{NaI}$  (2 moles) in 90% alc. refluxed 5 hrs. gives (80% yield (1))  $\beta$ -iodoethyl benzoate, b.p. 161-163° at 17 mm. (1).

*Chem. Soc.* 57, 571 (1935). (5) Sprague, Johnson, *J. Am. Chem. Soc.* 59, 1838-1839 (1937). (6) Wibaut, Heermann, Wagendonk, *Rec. trav. chim.* 57, 456-458 (1938). (7) Westphal, Jerchel, *Ber.* 73, 1004-1011 (1940). (8) Karrer, Kahnt, Epstein, Jaffé, Ishii, *Helv. Chim. Acta* 21, 233-234 (1938). (9) Vogel, *J. Chem. Soc.* 1943, 638, 641. (10) Meals, *J. Org. Chem.* 9, 211-218 (1944).

3:8820  $\gamma$ -PHENOXY-*n*-PROPYL CHLORIDE  $C_9H_{11}OCl$  Beil. VI-142  
( $\gamma$ -Chloro-*n*-propyl phenyl ether)   $OCH_2CH_2CH_2Cl$  VI<sub>1</sub>—

B.P.	M.P.	
245-255° (1)	11.8-12° (1)	$D_4^{20} = 1.1167$ (4)
238-240° at 745 mm. (2)		
139° at 25 mm. (3)		

Colorless oil gradually turning yellowish in light.

[For prepn. of  $\bar{C}$  from  $\gamma$ -phenoxy-*n*-propyl alcohol (trimethylene glycol monophenyl ether) [Beil. VI-147, VI<sub>1</sub>-(85)] with  $SOCl_2$  + pyridine (88% yield) see (3).]

[For prepn. of  $\bar{C}$  from 1-bromo-3-chloropropane (trimethylene glycol chlorobromide) (5) with potassium phenolate (1) or with alc. sodium phenolate (yields: 68% (6) (4), 55% (2)) see indic. refs.; note that by this method some trimethylene glycol diphenyl ether (1,3-diphenoxypropane) (1:7170), m.p. 61°, h.p. 338-340° cor., may also be formed.]


[ $\bar{C}$  with diethyl sodiomalonate in usual way gives (yields: 77% (2), 55% (6), 55% (4)) diethyl ( $\gamma$ -phenoxy-*n*-propyl)malonate [Beil. VI-168], h.p. 271° dec. at 140 mm. (4), 265-266° at 140 mm. (7), 216-219° at 20 mm. (6), m.p. 32° (7), 30° (4). — For analogous behavior of  $\bar{C}$  with diethyl sodio-methylmalonate see (7).]

[ $\bar{C}$  with Na in ether undergoes a complex decomposition giving (8) cf. (7) sodium phenolate, propylene, cyclopropane, hexamethylene glycol diphenyl ether, etc.]

[For study of rate of reactn. of  $\bar{C}$  with KI in acetone at 50° and at 60° see (3).]

— *N*-( $\gamma$ -Phenoxypropyl)phthalimide (phenyl  $\gamma$ -(phthalimido)-*n*-propyl ether) [Beil. XXI-472] ndls. from alc., m.p. 91° (9), 88° (10). [Not reported from  $\bar{C}$  but ohtd. in 80% yield (10) from  $\gamma$ -phenoxy-*n*-propylbromide with K phthahmide; also indirectly (9).]

3:8820 (1) Henry, *Bull. soc. chim.* (3) 15, 1224 (1896). (2) Gabriel, *Ber.* 25, 416-418 (1892). (3) Kirner, *J. Am. Chem. Soc.* 48, 2748-2749 (1926). (4) Granger, *Ber.* 28, 1198-1200 (1895). (5) Allen, *Org. Synth.* 1, 157 (1923). (6) Allen, *Org. Synth.* 1, 157 (1923). (7) Allen, *Org. Synth.* 1, 157 (1923). (8) Allen, *Org. Synth.* 1, 157 (1923). (9) Manske, *J. Am. Chem. Soc.* 65, 2570 (1943). (10) Allen, *Org. Synth.* 1, 157 (1923).

— 4-CHLORO-3,5-DIMETHYLPHENOL   $C_8H_7OCl$  Beil. VI —  
VI<sub>1</sub>—  
VI<sub>2</sub>-(463)

B.P. 246° M.P. 115°

See 3:3505. Division A: Solids.

Cryst. (from abs. alc.) with agreeable musk-like odor.

[For prepn. of  $\bar{C}$  from 2,7-dimethyloctanediol-2,7 [Beil. I<sub>1</sub>-(257)] with conc. HCl in the cold or with HCl gas in toluene see (1).]

3:0840 (1) Bouvet, *Bull. soc. chim.* (4) 17, 204 (1915).

3:0843 CHLORAL *n*-BUTYLALCOHOLATE  $C_6H_{11}O_2Cl_3$  Beil. I - 622  
(Trichloroacetaldehyde  $Cl_3C-CH-O-CH_2CH_2CH_2CH_3$  I<sub>1</sub>-  
*n*-butylhemiacetal)  $\begin{array}{c} | \\ OH \end{array}$  I<sub>2</sub>-

M.P. 49-50° (1) B.P. 129-130° at 742 mm. (3)

49° (2) (3) 129-130° cor. (1)

Colorless ndls.

[For prepn. of  $\bar{C}$  from anhydrous chloral (3:5210) with 1 mole *n*-butyl alcohol (1:6180) (1) (2), or from chloral hydrate (3:1270) under reflux with *n*-BuOH (yields: 54% in 45 min., 28% in 60 min. (3)) or with tri-*n*-butyl orthoformate, see indic. refs.; for study of formn. of  $\bar{C}$  from chloral ethylalcoholate (3:0860) or from chloral *n*-propyl-hemiacetal by reflux with *n*-BuOH for 45 min. (yield 40-50%) see (3).]

[ $\bar{C}$  with AcCl gives (78% yield (1)) corresp. acetate, b.p. 129-131° at 20 mm. (1).]

[For behavior of  $\bar{C}$  with diazomethane see (4).]

3:0843 (1) Fourneau, Florence, *Bull. soc. chim.* (4) 47, 352 (1930). (2) Kuntze, *Arch. Pharm.* 246, 98 (1908). (3) Post, *J. Org. Chem.* 6, 832-833 (1941). (4) Meerwein, Bersin, Burneleit, *Ber.* 62, 1009 (1929).

3:0844 2-CHLORO-3,5-DIMETHYLPHENOL  $C_8H_9OCl$  Beil. VI -  
(6-Chloro-*m*-5-xyleneol)  $\begin{array}{c} OH \\ | \\ \text{C}_6H_3(CH_3)_2Cl \end{array}$  VI<sub>1</sub>-  
VI<sub>2</sub>- (464)

M.P. 49-50° (1)

[For formn. of  $\bar{C}$  from 3,5-dimethylphenol (*sym*.-*m*-xyleneol) (1:1455) with  $SO_2Cl_2$  in  $CHCl_3$  (as by-product of the principal isomer 4-chloro-3,5-dimethylphenol (3:3505)) see (1).]

— 2-Chloro-3,5-dimethylphenyl acetate: unreported.

— 2-Chloro-3,5-dimethylphenyl benzoate: unreported.

3:0844 (1) Lesser, Gad, *Ber.* 56, 974 (1923).

3:0846 1,1,1-TRICHLOROPROPANOL-2  $C_3H_5OCl_3$  Beil. I - 365  
( $\beta,\beta,\beta$ -Trichloroisopropyl  $CH_3-CH-CCl_3$  I<sub>1</sub>-(185)  
alcohol; "Isopral")  $\begin{array}{c} | \\ OH \end{array}$  I<sub>2</sub>-(385)

M.P. 50-51° (1) B.P. 161.8° cor. at 774 mm. (5)

50° (2) (3) 161.8° at 773 mm. (1)

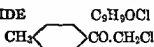
49.2° (4) (6) 63-65° at 20 mm. (19)

49° (5) 53-55° at 12 mm. (3)

46-49° (19)

Hexag. cryst. from aq. (7); for crystallographic data see (2). — Spar. sol. aq., eas. sol. org. solvents (for data see (7)). —  $\bar{C}$  has high vapor press. (for measurement see (2)) and sublimes even at ord. temp. (for study of sublimation of  $\bar{C}$  by various methods see (5)).



— *p*-METHYLPHENACYL CHLORIDEBeil. VII - 309  
VII<sub>1</sub>-(165)

B.P. 260-263°

M.P. 57-58°

See 3:1130. Division A: Solids.

## — 2-CHLOROHYDROQUINONE

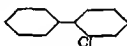
 $\text{C}_6\text{H}_5\text{O}_2\text{Cl}$ Beil. VI - 849  
VI<sub>1</sub>-(417)  
VI<sub>2</sub> (844)

B.P. 263°

M.P. 106°

See 3:3130. Division A: Solids.

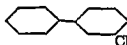
## — 2-CHLOROBIPHENYL

 $\text{C}_{12}\text{H}_9\text{Cl}$ Beil. V - 579  
V<sub>1</sub>-(272)  
V<sub>2</sub>-(483)

B.P. 274° at 738 mm.

M.P. 34°

See 3:0300. Division A: Solids.

3:8940 3-CHLOROBIPHENYL  
(3-Chloroxenene (1)) $\text{C}_{12}\text{H}_9\text{Cl}$ Beil. V - 579  
V<sub>1</sub>—  
V<sub>2</sub>-(483)

B.P. 284-285° (2) (6)

M.P. +16° (4)

150-160° at 6 mm. (3)

87° at 0.15 mm. (4)

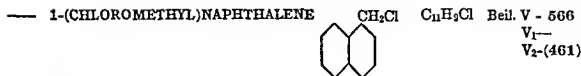
: Pale yel. oil. — By soln. in 2 vols. 96% alc., cooling to  $-18^\circ$ , and scratching,  $\bar{C}$  has been obtd. in colorless cryst. from. (4).

[For prepn. (27% yield (2), 16% yield (4), 13-25% yield (3)) from diazotized *m*-chloroaniline +  $\text{C}_6\text{H}_6$  see (3) (4) (2).]

$\bar{C}$  on oxidn. with  $\text{CrO}_3$  in  $\text{AcOH}$  +  $\text{V}_2\text{O}_5$  yields (5) *m*-chlorobenzoic acid (3:4392), m.p.  $154^\circ$ .

$\bar{C}$  on nitration (no details (6)) gives a dinitro compd., 3-chloro-4,4'-dinitrobiphenyl, wooly flocks from alc., m.p. 202-203° (6) (9). [No other dinitro-3-chlorobiphenyls are recorded; of the possible mononitro-3-chlorobiphenyls only two (both prepd. indirectly) are known, viz., 4-nitro-3-chlorobiphenyl, m.p. 78.5-79.5° (7), and 3'-nitro-3-chlorobiphenyl, m.p. 101° (8).]

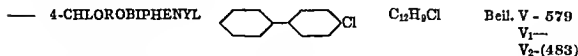
3:8940 (1) Hale, *J. Am. Chem. Soc.* 54, 4458-4459 (1932). (2), Gomberg, Bachmann, *J. Am. Chem. Soc.* 46, 2343 (1924). (3) Elks, Haworth, Hey, *J. Chem. Soc.* 1940, 1285 (4) Weissberger, Sängewald, *Z. physik. Chem. B-20*, 154 (1933). (5) Bellavita, *Cazz. chim. ital.* 65, 639 (1935). (6) Mascarelli, Gatti, *Cazz. chim. ital.* 63, 660 (1933). (7) Schoepfle, Truesdale, *J. Am. Chem. Soc.* 59, 376 (1937). (8) Mascarelli, Gatti, *Atti accad. sci. Torino*, 65, 143-147; *Cent.* 1930, II 1861. (9) Case, *J. Am. Chem. Soc.* 67, 116, 118 (1945).



B.P. 291-292°

M.P. 32°

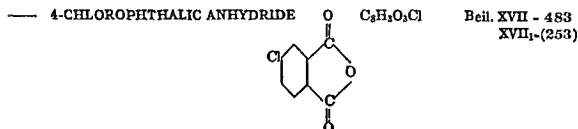
See 3:0250. Division A: Solids.



B.P. 291° at 745 mm.

M.P. 77°

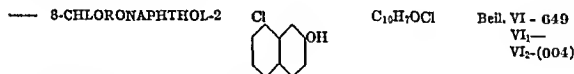
See 3:1912. Division A: Solids.



B.P. 294.5° cor. at 720 mm.

M.P. 98°

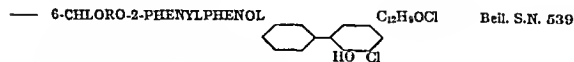
See 3:2725. Division A: Solids



B.P. 307-308°

M.P. 101°

See 3:2965. Division A: Solids.



B.P. 312° at 745 mm.

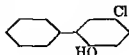
M.P. 71-72°

See 3:1757. Division A: Solids.

3:8980 4-CHLORO-2-PHENYLPHENOL  
(5-Chloro-2-hydroxybiphenyl)

 $C_{12}H_9OCl$ 

Beil. S.N. 539



B.P. 319° at 746 mm. (1)  
178° at 15 mm. (1)  
166-171° at 10 mm. (2)  
128-130° at 2 mm. (3)

M.P. +11° (1) (4)

[See also 6-chloro-2-phenylphenol (3:1757).]

Important Note: Through the year 1944 (and perhaps in some cases beyond) the chloro-phenylphenol of m.p. + 11° (C) was regarded as having the structure 6-chloro-2-phenylphenol = 3-chloro-2-hydroxybiphenyl. In 1945, however, this view was corrected by the paper of Weissberger and Salminen (3); in this text, therefore, expression of the facts is reported in the light of their paper. Particular care is, therefore, required in consulting references prior to it since such material is universally expressed in the reverse sense of the present view.

[For prepn. of C from 2-hydroxybiphenyl (1:1440) with  $Cl_2$  (note that 6-chloro-2-phenylphenol (3:1757) is also formed) see (1) (4) (3), for prepn. of C from 5-amino-2-hydroxybiphenyl (5) by diazotization and use of  $Cu_2Cl_2$  reaction (27% yield (3)) see indic. refs.]

C is sol. in aq. 25% NaOH at 60° but on cooling seps.  $Na\bar{A}\cdot 4H_2O$ , m.p. 84-85° (1); anhydrous  $Na\bar{A}$ , m.p. 280° (1) (4) (for use in sepn. of C from the isomeric 6-chloro-2-phenylphenol (3:1757) see (1)). [For formn. of  $Na\bar{A}$  in org. solvents such as MeOH, ether, or toluene see (8).]

The calcium salt of C is more sol. in aq. than the corresp. deriv. of the isomeric 6-chloro-2-phenylphenol (3:1757) (use in sepn. (2)).

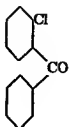
C on mononitration with  $HNO_3$  in AcOH at 15-20° as directed gives (48% yield (3)) 5-chloro-2-hydroxy-3-nitrobiphenyl, yellow ndls., m.p. 57-58° (3).

[C on condensation with formaldehyde + morpholine yields (6) a prod. m.p. 125-125° (6).]

— 4-Chloro-2-phenylphenyl benzoate: m.p. 86-87° (7). [Note that this prod. does not distinguish C from the isomeric 6-chloro-2-phenylphenol (3:1757) whose benzoate has m.p. 88.5°.]

3:8980 (1) Britton, Bryner (to Dow Chem. Co.), U.S. 1,921,727; Aug. 8, 1933; *Cent.* 1934, I 128-129; *C.A.* 27, 5086 (1933); *Brit.* 396,251, Aug. 24, 1933; *Cent.* 1934, I 128-129; *C.A.* 28, 578 (1934). (2) Rittler, Heller (to Chem. Fabrik von Heyden), Ger. 615,133, June 27, 1935; *Cent.* 1936, I 884; *C.A.* 29, 6347 (1935). (3) Weissberger, Salminen, *J. Am. Chem. Soc.* 67, 58-60 (1945). (4) Britton, Bryner (to Dow Chem. Co.), U.S. 1,969,963, Aug. 14, 1934; *C.A.* 28, 6160 (1934). (5) Vorozhtsov, Troshchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 431-437 (1938); *Cent.* 1940, II 2152; *C.A.* 32, 7907 (1938). (6) Bruson (to Rohm and Haas Co.), U.S. 2,040,039, May 5, 1936; *Cent.* 1936, II 1386-1387; *C.A.* 30, 4177 (1936). (7) Harris, Christiansen, *J. Am. Pharm. Assoc.* 24, 553-557 (1935). (8) Mills (to Dow Chem. Co.), U.S. 1,955,080, April 17, 1934; *Cent.* 1934, II 1991; *C.A.* 28, 3743 (1934).

## — 2-CHLOROBENZOPHENONE

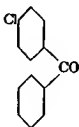
 $C_{13}H_9OCl$ Beil. VII - 419  
VII<sub>1</sub>-(227)

B.P. 330° cor.

M.P. 45-46°

See 3:0715. Division A: Solids.

## — 4-CHLOROBENZOPHENONE

 $C_{13}H_9OCl$ Beil. VII - 419  
VII<sub>1</sub>-(227)

B.P. 332° at 771 mm.

M.P. 77-78°

See 3:1014. Division A: Solids.



## CHAPTER XX

### DIVISION C. LIQUIDS WITH BOILING POINTS REPORTED ONLY UNDER REDUCED PRESSURE

3:9000-3:9299 (C<sub>3</sub>-C<sub>6</sub> inclusive)

(Arranged in sequence of empirical formulas)

3:9030 MALONYL DICHLORIDE		$\begin{array}{c} \text{O}=\text{C}-\text{CH}_2-\text{C}=\text{O} \\   \qquad \qquad   \\ \text{Cl} \qquad \qquad \text{Cl} \end{array}$	C <sub>3</sub> H <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub>	Beil. II - 582 II <sub>1</sub> -(252) II <sub>2</sub> -(529)
B.P. 58°	at 27 mm. (1) (2) (3)	D <sub>4</sub> <sup>22.5</sup> = 1.4505 (4)	n <sub>D</sub> <sup>23.4</sup> = 1.45973 (4)	
58°	at 26 mm. (4)			
53.6°	at 22 mm. (5)	D <sub>4</sub> <sup>20</sup> = 1.4509 (5)		
53-54°	at 19 mm. (4)	1.450 (4)	n <sub>D</sub> <sup>20</sup> = 1.4639 (5)	
55°	at 15 mm. (6)			
47°	at 15 mm. (7)	D <sub>4</sub> <sup>18.6</sup> = 1.4486 (4)	n <sub>D</sub> <sup>18.4</sup> = 1.46205 (4)	
47°	at 13 mm. (4)			

Colorless liq. turning dark red on stdg. (6).

[For prepn. of  $\bar{\text{C}}$  from malonic acid (1:0480) with SOCl<sub>2</sub> (yield 70% (8), 60% (6), 50% (9)) (1) (2) or with PCl<sub>5</sub> (yield: 68% (3), 36% (7)) see indic. refs.; for formn. of  $\bar{\text{C}}$  from carbon suboxide with dry HCl gas see (10); for mfg. of  $\bar{\text{C}}$  from methylene dichloride (3:5020) with CO, COS, or COCl<sub>2</sub> (3:5000) + cat. at 700° see (11).]

[ $\bar{\text{C}}$  in ether or EtOAc with Ag<sub>2</sub>O, PhO, ZnO, etc., yields (8) carbon suboxide, b.p. +7°;  $\bar{\text{C}}$  treated at 0° with dry HBr gas yields (12) malonyl dibromide, b.p. 55-57° at 11 mm. (12);  $\bar{\text{C}}$  on cat. hydrogenation as specified (13) yields a condensation prod., m.p. 83°, of formylglutaconic acid.]

[ $\bar{\text{C}}$  with acetone + CaCO<sub>3</sub> yields (14) mainly CH<sub>3</sub>.CO.CH<sub>2</sub>.CO.CH<sub>2</sub>.CO.Cl [Beil. III- (263)] + a little phloroglucinol (1:1620) (the acid chloride itself, however, is quant. conv. to phloroglucinol by further htg. with CaCO<sub>3</sub>).]

[ $\bar{\text{C}}$  with AlCl<sub>3</sub> + C<sub>6</sub>H<sub>6</sub> yields (1) dibenzoylmethane (1:1480), m.p. 78°; for reactn. of  $\bar{\text{C}}$  with AlCl<sub>3</sub> + naphthalene (1:7200) yielding (15) (16) *peri*-naphthindandione (1,8-malonylnaphthalene) [Beil. VII- (391)] see indic. refs.; for reactn. of  $\bar{\text{C}}$  with acenaphthene (1:7225) yielding (15) (17) *peri*-acenaphtheneindandione (5,6-malonylacenaphthene) which on oxidn. gives (17) (18) naphthalene-1,4,5,8-tetracarboxylic acid [Beil. IX-1002,

longer evolved gives (85% yield (19)) malonyl-diurethane, cryst. from alc., m.p. 124° (19).  $\bar{\text{C}}$  on hydrolysis with aq. yields malonic acid (1:0480). [Note that the half acid chloride of malonic acid has m.p. 65° dec. (20).] — For the amide, anilide, p-toluidide, and other derivs. corresp. to  $\bar{\text{C}}$  see malonic acid (1:0480).

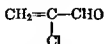
3:9030 (1) Auger, *Ann. chim.* (6) 22, 347-350 (1891). (2) Asher, *Ber.* 30, 1023-1024 (1897). (3) Clark, *Bell. Trans. Roy. Soc. Can.* (3), 27, 111 97-107 (1933). (4) von Auwers, Schmidt, *Ber.* 46, 477-478 (1913). (5) Martin, Partington, *J. Chem. Soc.* 1936, 1181. (6) McMaster, Ahmann, *J. Am. Chem. Soc.* 50, 146 (1928). (7) Black, Shaw, Walker, *J. Chem. Soc.* 1931, 276. (8) *Chem. Soc. Trans.* 1908, 416. (9) Nightingale, Alexander, *J. Am. Chem. Soc.* 28, 696 (1906).

Oil Development Co.), U.S. 2,062,344, Dec. 1, 1936;

(12) Fleischer, Hittle, Wolff, *Ber.* 53, 1848 (1920).

(13) Fröschl, Maier, *Monatsh.* 59, 261, 269-270 (1928). (14) Komninos, *Compt. rend.* 167, 781 (1918); *Bull. soc. chim.* (4) 23, 452-455 (1918). (15) Fleischer, Retze, *Ber.* 55, 3282, 3285 (1922). (16) Badische Anilin und Soda Fabrik, Ger. 233,365, Apr. 10, 1915; *Cent.* 1915, 1 965. (17) Eckert (to I.G.), Ger. 439,511, Jan. 14, 1927, *Cent.* 1927, 1 1527. (18) Eckert (to Grasselli Dye-stuffs Corp.), U.S. 1,612,103, Dec. 28, 1926; *Cent.* 1927, 1 1527, *C.A.* 21, 593 (1927). (19) Baster-field, Woods, Whelen, *J. Am. Chem. Soc.* 49, 2945 (1927). (20) Staudinger, Ott, *Ber.* 41, 2211-2212 (1908).

3:0031  $\alpha$ -CHLOROACROLEIN  
(2-Chloropropen-2-al-1)



Beil. I —

I<sub>1</sub> —

I<sub>2</sub>-(785)

B.P. 40° at 30 mm. (1)

$D_4^{20} = 1.199$  (2) (3)

$n_D^{20} = 1.463$  (2) (3)

39-40° at 30 mm. (2)

$D_4^{15} = 1.205$  (3)

29-31° at 17 mm. (3)

$D_4^0 = 1.272$  (3)

Colorless strongly lachrymatory liq. with pronounced irritating effect on mucous membranes.

[For prepn. of  $\tilde{\text{C}}$  from nerolein (1:0115) in aq. with  $\text{Cl}_2$  (50% yield (2)) or from  $\alpha,\beta$ -dichloropropionaldehyde (3:9034) by loss of 1 HCl with hot aq. NaOAc (27% yield (3)) (1) see indic. refs.]

$\tilde{\text{C}}$  readily polymerizes.

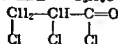
[ $\tilde{\text{C}}$  in  $\text{CCl}_4$  with  $\text{Cl}_2$  in cold adds 1 mole halogen giving (2)  $\alpha,\alpha,\beta$ -trichloropropionaldehyde (3:9033).]

[ $\tilde{\text{C}}$  in dry ether with  $\text{Br}_2$  in cold adds 1 mole halogen giving (2)  $\alpha$ -chloro- $\alpha,\beta$ -dibromopropionaldehyde, b.p. 105° at 55 mm.,  $D_4^{20} = 2.17$ ,  $n_D^{20} = 1.548$ .]

[For conversion of  $\tilde{\text{C}}$  with EtOH to  $\alpha$ -chloroacrolein diethylacetal, b.p. 158-160°, see (4).]

3:9031 (1) Muskat, Becker, *J. Am. Chem. Soc.* 52, 816-817 (1930). (2) Berlande, *Bull. soc. chim.* (4) 37, 1392-1393 (1925). (3) Moureu, Robin, Boismenu, *Ann. chim.* (9) 15, 210-211 (1921). (4) The Distillers Co., Ltd., Staudinger, Tuerck, Lichtenstein, *Brit.* 554,570, July 9, 1913; *C.A.* 33, 312 (1945).

3:0032  $d,l$ - $\alpha,\beta$ -DICHLOROPROPIONYL CHLORIDE  $\text{C}_3\text{H}_2\text{OCl}_3$  Beil. S.N. 162



B.P. 52-54° at 16 mm. (1)

$D_4^{20} = 1.4757$  (2)

$n_D^{20} = 1.47640$  (2)

43-44° at 10 mm. (2)

[For prepn. of  $\tilde{\text{C}}$  from  $\alpha,\beta$ -dichloropropionic acid (3:0855) with  $\text{SOCl}_2$  see (1) (2); for formn. of  $\tilde{\text{C}}$  from glyceric acid ( $\alpha,\beta$ -dihydroxypropionic acid) with  $\text{PCl}_5$  see (4) (3) (5).]

[ $\tilde{\text{C}}$  with alcohols yields alkyl  $\alpha,\beta$ -dichloropropionates; e.g., cf. (1) (2) (3).]

$\tilde{\text{C}}$  on hydrolysis yields  $\alpha,\beta$ -dichloropropionic acid (3:0855) q.v.

3:9032 (1) Marvel, Dec, Cooke, Cowan, *J. Am. Chem. Soc.* 62, 3495-3498 (1940). (2) Leimu, *Ber.* 70, 1016, 1050 (1937). (3) Werigo, Werner, *Ann.* 170, 163-167 (1874). (4) Werigo, Okubtch, *Ann.* 167, 49 (1873). (5) Wiechelhaus, *Ann.* 135, 253 (1865); 143, 3 (1867).

[ $\bar{C}$  with hexanone-2 directly has not been studied, but  $\bar{C}$  with *n*-butylacetylene (1:8055) in pres. of  $\text{Et}_2\text{O} \cdot \text{BF}_3 / \text{HgO} / \text{MeOH} / \text{trichloroacetic acid}$  gives (104) 4-(chloromethyl)-2-*n*-butyl-2-methyl-1,3-dioxolane, h.p.  $109^\circ$  at 25 mm.]

[ $\bar{C}$  with acetophenone (1:5515) in pres. of  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  gives (105) a prod. presumably 4-(chloromethyl)-2-methyl-2-phenyl-1,3-dioxolane, b.p.  $153\text{--}153.3^\circ$  at 40 mm., which with 2 *N*  $\text{HCl}$  at  $60^\circ$  is hydrolyzed into its original components.]

#### BEHAVIOR OF $\bar{C}$ WITH SALTS OF ORGANIC ACIDS

$\bar{C}$  reacts with salts of organic acids to give in general the corresp. glycerol  $\alpha$ -esters.

With salts of aliphatic monohasic acids. [ $\bar{C}$  with Na formate on htg is claimed to yield (106) (45) glycerol  $\alpha$ -monoformate [Beil. II-24, II<sub>1</sub>-(19), II<sub>2</sub>-(33)], but owing to the instability of this prod. the reliability of its supposed constants has been questioned (8) ]

[ $\bar{C}$  with NaOAc or KOAc in s.t. at  $150\text{--}160^\circ$  yields (107) glyceryl  $\alpha$ -acetate [Beil. II-146, II<sub>1</sub>-(69), II<sub>2</sub>-(159)], h.p.  $129\text{--}131^\circ$  at 3 mm.,  $D_4^{20} = 1.2060$ ,  $n_D^{20} = 1.4517$  (108), but the reactn. is accompanied by some formn of glyceryl diacetate and glyceryl triacetate.]

[For corresp. reactions of  $\bar{C}$  with sodium salts of *n*-butyric acid (1:1035), isobutyric acid (1:1030), *n*-valeric acid (1:1060), isovaleric acid (1:1050), and *n*-caproic acid (1:1130) see (8).]

[ $\bar{C}$  with K laurate in s.t. at  $180^\circ$  under  $\text{CO}_2$  (109) or  $\bar{C}$  with Na laurate at  $130^\circ$  (110) gives glyceryl  $\alpha$ -laurate ("  $\alpha$ -monolaurin ") [Beil. II-362, II<sub>1</sub>-(157), II<sub>2</sub>-(320)], m.p.  $63^\circ$  (111), cf. (112),  $62^\circ$  (2).]

[ $\bar{C}$  with K myristate in s.t. at  $180^\circ$  under  $\text{CO}_2$  (109), or  $\bar{C}$  with sodium myristate at  $110\text{--}115^\circ$  for 8-10 hrs. (110), gives (70% yield (110)) glyceryl  $\alpha$ -myristate ("  $\alpha$ -monomyristin ") [Beil. II-366, II<sub>1</sub>-(162), II<sub>2</sub>-(327)], m.p.  $68^\circ$  (109) (113),  $67.3^\circ$  (111) cf. (112).]

[ $\bar{C}$  with K palmitate in s.t. at  $180^\circ$  under  $\text{CO}_2$  (109), or  $\bar{C}$  with Ph palmitate at  $112^\circ$  under  $\text{CO}_2$  (113), gives (50% yield (113)) glyceryl  $\alpha$ -palmitate ("  $\alpha$ -monopalmitin ") [Beil. II-373, II<sub>2</sub>-(338)], m.p.  $74\text{--}75^\circ$  (2),  $77^\circ$  (111) cf. (112).]

[ $\bar{C}$  with K stearate in s.t. at  $180^\circ$  under  $\text{CO}_2$  (109), or  $\bar{C}$  with sodium stearate at  $110\text{--}115^\circ$  for 8-10 hrs. (110) cf. (114), gives glyceryl  $\alpha$ -stearate ("  $\alpha$ -monostearin "), m.p.  $81.1^\circ$  (111) cf. (112).]

With salts of amino acids. [For analogous formn. of corresp. glyceryl mono esters from  $\bar{C}$  with sodium salts of aminoacetic acid (glycine) (115),  $\alpha$ -aminopropionic acid (alanine) (115),  $\alpha$ -amino-isocaproic acid (leucine) (116) see indic. refs ]

With alkali cyanides. [ $\bar{C}$  in 95% alc. with aq. KCN (or NaCN) in s.t. at  $100^\circ$  for 36 hrs., followed by hydrolysis, gives (9) 28% yield of the lactone of  $\beta,\gamma$ -dihydroxy-*n*-butyric acid ( $\beta$ -hydroxy-*n*-butyro- $\gamma$ -lactone), m.p.  $22.5\text{--}26^\circ$  (9), accompanied by (23% yield (9)) the lactone of  $\gamma$ -hydroxyisocrotonic acid, m.p.  $+5^\circ$  (9) (presumably formed by loss of  $\text{H}_2\text{O}$  from the former).] Cf. behavior of " glycerol  $\beta$ -monochlorohydrin " (3:9039).

#### BEHAVIOR OF $\bar{C}$ WITH OTHER NON-NITROGENOUS ORGANIC REACTANTS

With alkyl halides (or their equivalents). [ $\bar{C}$  with MeI + silver oxide (15), or  $\bar{C}$  with methyl *p*-toluenesulfonate at  $150^\circ$  for 5 hrs. (117), or  $\bar{C}$  with diazomethane (118) gives the corresp. dimethyl ether, viz., 3-chloro-1,2-diethoxypropane, h.p.  $156\text{--}157^\circ$  at 760 mm. (117),  $156\text{--}158^\circ$  (118),  $156^\circ$  (15),  $D_4^{25} = 1.08$  (15),  $n_D^{25} = 1.43$  (15).]

[Note that the corresp. diethyl ether, viz., 3-chloro-1,2-diethoxypropane, h.p.  $69.8\text{--}70.4^\circ$  at 14 mm.,  $D_4^{10} = 1.026$ ,  $n_D^{20} = 1.4246$ , has been prepd. indirectly (119).]

With  $\text{RMgX}$  cpds. [ $\bar{C}$  with  $\text{EtMgBr}$  (2 moles) reacts in an obscure fashion yielding (119) (45) 5455). —  $\bar{C}$  with *iso*- $\text{AmMgBr}$  (4 moles) (perhaps acting as (25% yield (120)) 2,5-dimethylhexanediol-1,2 [Beil. II-373, II<sub>2</sub>-(338)],  $129\text{--}132^\circ$  at 11 mm.]

[ $\bar{C}$  with  $C_6H_5MgBr$  (4 moles) (perhaps acting through intermediate acetol) gives (120) (121) (60% yield (120)) 2-phenylpropanediol-1,2 [Beil. VI-930] accompanied by some 3-phenylpropanediol-1,2 [Beil. VI-929].]

#### BEHAVIOR OF $\bar{C}$ WITH AMINES

With primary amines. *With aliphatic primary amines.* [ $\bar{C}$  with *n*-heptadecylamine (122) or its hydrochloride gives a prod. which may be the expected *N*-( $\beta,\gamma$ -dihydroxy-*n*-propyl)*n*-heptadecylamine.]

*With aromatic primary amines.* [ $\bar{C}$  with aniline (2 moles) + a little aq. refluxed for 1 hr., then neutralized, gives (63% yield (124)) *N*-( $\beta,\gamma$ -dihydroxy-*n*-propyl)aniline [Beil. XII-183], b p. 249–250° at 50 mm. (125), 200–203° (124), m p. 42° (124), 52° (125).]

[ $\bar{C}$  with *p*-aminophenol gives (126) *N*-( $\beta,\gamma$ -dihydroxy-*n*-propyl)-*p*-aminophenol, m.p. 192°, used as photographic developer (127); for analogous reactions of  $\bar{C}$  with *p*-anisidine giving *N*-( $\beta,\gamma$ -dihydroxy-*n*-propyl)-*p*-anisidine, m.p. 75–76° see (126), or of  $\bar{C}$  with *p*-phenetidine giving *N*-( $\beta,\gamma$ -dihydroxy-*n*-propyl)-*p*-phenetidine, m.p. 93° (126), 90–92° (128), see indic. refs.]

With secondary amines. *With aliphatic secondary amines* [ $\bar{C}$  with  $Me_2NH$  + aq. NaOH at 20–40° (129) or  $\bar{C}$  with  $Me_2NH$  in s.t. at 100° for 5–6 hrs. (130) (131) cf. (132) gives 3-(dimethylamino)propanediol-1,2 [Beil. IV-302], h.p. 220° cor. at 749 mm. (130), 111° at 15 mm. (132) —  $\bar{C}$  with  $Et_2NH$  in s.t. at 100° for 5–6 hrs. (131) cf. (130) (132) gives 3-(diethylamino)propanediol-1,2 [Beil. IV-302], b p. 233–235° at 748 mm (130) (131), 106° at 3 mm. (132) (corresp. bis-(*N*-phenylcarbamate), m.p. 106.5° (133); corresp. bis-(*N*-phenylcarbamate)monohydrochloride, m.p. 109° (133)).]

*With heterocyclic secondary amines* [ $\bar{C}$  with piperidine in s.t. at 100° for 4–5 hrs. (131, cf. (132) or in ord. flask at 100° for 1½ hrs. (134) gives 3-(piperidino)propanediol-1,2 [Beil. XX-34, XX-1-(12)], m.p. 83° (135) (132), 79–80° (136), 67–68° (134) (corresp. bis-(*p*-nitrobenzoate), m.p. 108° (135); corresp. bis-(*N*-phenylcarbamate)monohydrochloride ("Diothane"), m.p. 201–202° cor. (137), 197–198° u.c. (?) (133)). — Note that in prepn. of "Diothane" the influence of the purity of the piperidine has been studied (137); that 3-(piperidino)propanediol-1,2 yields a *mono*-(*N*-phenylcarbamate)monohydrochloride, m.p. 176–177° (133); for resolution of *d,l*-3-(piperidino)propanediol-1,2 into its opt. act. enantiomorphs and prepn. of the corresp. opt. act. "Diothanes" see (138) ]

With tertiary amines. [ $\bar{C}$  with  $Me_3N$  anhydrous (139) or in aq. soln. in s.t. at 100° for 8 hrs. (31) or in alc. soln. in s.t. at 100° for 6 hrs. (140) gives trimethyl-( $\beta,\gamma$ -dihydroxy-*n*-propyl)-ammonium chloride [Beil. IV-302]. —  $\bar{C}$  with  $Et_3N$  in s.t. at 100° for 8 hrs. gives (141) triethyl-( $\beta,\gamma$ -dihydroxy-*n*-propyl)-ammonium chloride [Beil. IV-303]. — For analogous behavior of  $\bar{C}$  with tri-*n*-propylamine, quinine, and strychnine see (141). — For quat. salt from  $\bar{C}$  with *N,N*-dimethyl "stenyl" amine see (142).]

#### BEHAVIOR OF $\bar{C}$ WITH OTHER NITROGENOUS ORG. REACTANTS

[ $\bar{C}$  with diazomethane gives (118) the corresp. dimethyl ether for which see above under behavior of  $\bar{C}$  with alkyl halides.]

[ $\bar{C}$  with aq.  $Na_2NCN$  stood for 12 hrs., then shaken with benzoyl chloride, gives (143) the trihenzoate, m.p. 130° of 5-(hydroxymethyl)-2-aminooxazoline; substitution of benzenesulfonyl chloride for the benzoyl chloride yields (144) corresp. *tris*-(benzenesulfonate), m.p. 158°.] Cf. behavior of epichlorohydrin (3:5358).

— Glycerol  $\alpha$ -monochlorohydrin  $\alpha'$ -acetate ( $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl acetate): h.p. 240° (see 3:6775).

- Glycerol  $\alpha$ -monochlorohydrin  $\beta$ -acetate ( $\beta$ -chloro- $\beta'$ -hydroxy-isopropyl acetate): b.p. 218° (see 3:6517).
- Glycerol  $\alpha$ -monochlorohydrin  $\alpha,\beta$ -diacetate: b.p. 245° (see 3:6840).
- Glycerol  $\alpha$ -monochlorohydrin  $\alpha'$ -benzoate: unreported.
- Glycerol  $\alpha$ -monochlorohydrin  $\beta$ -benzoate: unreported.
- Glycerol  $\alpha$ -monochlorohydrin  $\alpha',\beta$ -dibenzoate: unreported.
- ① Glycerol  $\alpha$ -monochlorohydrin di-( $p$ -nitrobenzoate): m.p. 108–109° u.c. (14), 108° (15), 107–108° (2). [From  $\bar{C}$  with  $p$ -nitrobenzoyl chloride (2 moles) in pyridine at room temp. for several days (93–96% yield (14)) or in  $\text{CHCl}_3$  soln. with quinoline as acid acceptor (100% yield (2)); note that this prod. depresses m.p. (121–122°) of the corresp. deriv. of the isomeric glycerol  $\beta$ -monochlorohydrin (3:9039) (14).]
- Glycerol  $\alpha$ -monochlorohydrin  $\alpha'$ -(?)-(N-phenylcarbamate): m.p. 123–129° (16), 127–129° (9), 126° (42). [From  $\bar{C}$  with phenyl isocyanate in 7% yield (9); note that for the corresp. deriv. of glycerol  $\beta$ -monochlorohydrin (3:9039) the m.p. is 133–136°.]
- ① N-( $\beta,\gamma$ -dihydroxy-n-propyl)phthalimide: m.p. 111.5–112.5° (145), 111° (46). [From  $\bar{C}$  with K phthalimide (100% yield (46)), but no details of conditions are stated.]

3:9038 (1) Fairbourn, Gibson, Stephens, *J. Soc. Chem. Ind.* 49, 1021–1023 (1930). (2) Fair-

(1931). (10) Gibson, *J. Soc. Chem. Ind.* 50, 971 (1931).

(11) Walden, Swinne, *Z. physik. Chem.* 79, 721 (1912). (12) Sjöberg, *Svensk Kem. Tid.* 53, 5berg, *Svensk Kem. Tid.* 54, 775–776  
Chem. Soc. 54, 775–776  
–452. (16) Rider, Hill,  
17, 67–75 (1879). (18)  
Chem. Ind. 50, 949–954

(1931). (20) Sturgis (to General Explosives Co.), U.S. 1,473,685, Nov. 13, 1923, *Cent.* 1924, I 720; C.A. 18, 472 (1924).

(21) Wrightsman (to du Pont Co.), U.S. 1,751,377, March 18, 1930; *Cent.* 1930, II 2476; C.A. 24, 2605 (1930); U.S. 1,891,255, Dec. 20, 1932; *Cent.* 1933, I 1717; C.A. 27, 2036 (1933). (22) Rosenthal (to F. Bayer & Co.), Ger. 406,426, Nov. 18, 1924; *Cent.* 1925, I 908; not in C.A. (23) Schütz, *Cellulosechem.* 19, 33–38 (1941); C.A. 36, 5008 (1942). (24) I G., Brit. 474,677, Dec. 2, 1937; *Cent.* 1938, I 2045, C.A. 32, 3064 (1938); French 805,557, Nov. 24, 1936; *Cent.* 1937, I 3397; C.A. 31, 4417 (1937). (25) Cla  
*Cent.* 1935, I 2548; C.A. 29, 11:  
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(29) Conant, Quayle, *Org. Synth.*  
(1932); 2, 33–35 (1922). (30) 1  
(1854).

(31) Hanriot, *Ann. chim.* (5) 17, 80, 100, 114 (1879). (32) Nivière, *Compt. rend.* 156, 1623

6, 1680 (1912).  
A.G.,  
1914;  
7, 899,  
1920).  
1655  
C.A.  
Söhne,  
1908).  
C.A.

(41) Deutsche Sprengstoff, A.G., Ger. 229,872, Jan. 6, 1911; *Cent.* 1911, I 358; C.A. 5, 2557 (1911); Ger. 229,536, Dec. 22, 1910; *Cent.* 1911, I 274; C.A. 5, 2557 (1911); Ger. 201,230, Sept. 25, 1908; *Cent.* 1908, II 1218; C.A. 3, 377 (1910). (42) Carré, Mauclore, *Compt. rend.* 102, 1568 (1931). (43) Brönsted, Mary Kilpatrick, Martin Kilpatrick, *J. Am. Chem. Soc.* 51, 430–431, 445–446 (1929). (44) Fourneau, Ribas y Marques, *Bull. soc. chim.* (4) 39, 700 (1920). (45) Delaby,

[For prepn. of  $\bar{C}$  from 1,1,1-trichloropropanone-2 (3:5020) by reduction with fused  $Al(OEt)_3$  in abs. alc. under  $H_2$  or  $N_2$  (8) or with  $AlEt_3$  etherate in ether (3) (yields: 67% (8), 65% (3)) see indic. refs.; for prepn. of  $\bar{C}$  from chloral (3:5210) with  $CH_3MgBr$  (9) (19) (2) cf. (4) or  $MeMgI$  (2) cf. (4) (yield: 40% (9) (2)) see indic. refs. (note that by this method the normal addn. of  $RMgX$  leading to  $\bar{C}$  is accompanied by reduction leading to 2,2,2-trichloroethanol (3:5775) and the relative proportion of these two reactions is profoundly influenced by the pres. of metal salts (9)); for prepn. of  $\bar{C}$  from chloral (3:5210) with  $ZnMe_2$  see (6) ]

$\bar{C}$  is used as hypnotic pharmaceutical under the trade name "Isopral" (10), for use as seed disinfectant see (11); for study of disinfectant power and toxicity see (12); for comparative study of narcotic action see (13) — For study of tests for  $\bar{C}$  see (7) (14).

$\bar{C}$  on reduction in aq.  $AcOH$  +  $Zn$  dust in cold yields (15) 1,1-dichloropropene-1 (3:5120).  $\bar{C}$  on oxidn. with fuming  $HNO_3$  under reflux for 5 hrs. gives (2) trichloroacetic acid (3:1150); use of  $K_2Cr_2O_7$  +  $H_2SO_4$  gives only insignificant yields (2) while less strong  $HNO_3$  even after 4 hrs. at  $100^\circ$  has only slight action (2).

$\bar{C}$  with  $P_2O_5$  on htg. loses  $H_2O$  giving (84% yield (19)) (2) 1,1,1-trichloropropene-2 (3:5345), b.p.  $114-115^\circ$  at 757 mm. (2).

[ $\bar{C}$  with  $HNO_3/H_2SO_4$  mixt. yields (2)  $\beta,\beta,\beta$ -trichloroisopropyl nitrate, oil,  $D_{15}^{20} = 1.499$ ,  $n_D^{20} = 1.47892$ , but decomp. on htg. —  $\bar{C}$  with  $PCl_3$  or  $PCl_5$  yields (2) (1) various partial ester/acid chloride derivs. of phosphorous or phosphoric acids —  $\bar{C}$  with  $SOCl_2$  evolves  $HCl$  +  $SO_2$  and also yields (2) a liq. presumably  $\beta,\beta,\beta$ -trichloroisopropyl chlorosulfonate.]

$\bar{C}$  with aq. or alc.  $NaOH$  or conc. aq.  $Na_2CO_3$  gives on htg. (16) (17) mainly acetaldehyde (1:0100) and lactic acid (1:0400), also accompanied by formic acid (1:1005) and carbon monoxide; for use of this reactn. in detection of  $\bar{C}$  see (14) —  $\bar{C}$  with  $EtOH/NaOEt$  on htg. gives (15) ethyl  $\alpha$ -ethoxypropionate [Bul. III-280, III-1(109), III-2(206)], b.p.  $155^\circ$  cor. at 760 mm.,  $D_4^{20} = 0.9446$ ,  $n_D^{20} = 1.40125$ .

[ $\bar{C}$  with  $AcCl$  yields (2)  $\beta,\beta,\beta$ -trichloroisopropyl acetate, b.p.  $180-181^\circ$  cor. 766 mm., m.p. +  $8^\circ$ ,  $D_{15}^{20} = 1.353$ ,  $n_D^{20} = 1.46017$  (2).]

—  $\beta,\beta,\beta$ -Trichloroisopropyl carbamate: cryst. from  $C_6H_6$ , m.p.  $125^\circ$  (18). Prepd. indirectly from  $\beta,\beta,\beta$ -trichloroisopropoxy  $MgBr$  with phosgene in toluene, followed by treatment with  $NH_3$  (35% yield (18)).]

3:0846 (1) Henry, *Compt. rend.* 133, 205 (1904). (2) Vitoria, *Rec. trav. chim.* 24, 265-287 (1905); *Bull. acad. roy. Belg* 1904, 1087-1123; *Cent.* 1905, I 344-345. (3) Meerwein, Hinz, Majert, *Sohnke, J. prakt. Chem.* (2) 147, 236-237 (1936). (4) Bayer and Co., Ger. 151,545, May 20, 1904; *Cent.* 1904, I 1586. (5) Eder, Haas, *Mikrochemie (Emich Festschrift)*, 1930, 59, 67, 78, 80. (6) Garzaroli-Thurnlackh, *Ann.* 210, 77-79 (1881). (7) Genot, *J. pharm. Belg* 12, 735-736 (1930); *Cent.* 1930, II 3062. (8) Meerwein, Schmidt, *Ann.* 444, 234 (1925). (9) Kharasch, Kleiger, Martin, Mayo, *J. Am. Chem. Soc.* 63, 2306-2307 (1941). (10) *Cent.* 1903, II 899.

(11) von Leuthold, *Austrian* 145,527, May 11, 1936, *Cent.* 1936, II 1052. (12) Howard, Stimpert, *J. Am. Pharm. Assoc.* 14, 487-489 (1925), *Cent.* 1925, II 1696, *C.A.* 19, 2864 (1925). (13) Lendle, *Arch. expil. Path. Pharmacol.* 125, 287-300 (1937), *Cent.* 1928, I 715; *C.A.* 23, 839 (1928). (14) Serantes, *Anales soc. quim. argentina* 12, 199-200 (1924), *C.A.* 19, 704 (1925). (15) Wohl, *Roth, Ber.* 40, 215-216 (1907). (16) Hebert, *Bull. soc. chim.* (4) 27, 49 (1920). (17) Mosler, *Monatsh.* 29, 583-590 (1908). (18) Yoder, *J. Am. Chem. Soc.* 45, 479 (1923). (19) Kharasch, Rossin, Fields, *J. Am. Chem. Soc.* 63, 2559-2560 (1941).

wein, Hinz, *Ann.* 484, 17-18 (1930). (119) Meerwein, Hinz, Hofmann, Kroning, Pfeil, *J. prakt. Chem.* (2) 147, 278 (1936/7). (120) Grignard, *Compt. rend.* 141, 45 (1905); *Ann. chim.* (8) 10, 31-40 (1907).

(121) Grignard, *Ger.* 164,883, Nov. 16, 1905; *Cent.* 1905, II 1751. (122) I.G., *Brit.* 358,114, Oct. 29, 1931; *Cent.* 1932, I 1.

[C.A. 26, 2288  
*Cent.*, 1935, II

(1894). (126) Kolshorn, *Ger.* 346,385, Dec. 29, 1921, *Ger.* 346,386, Jan. 2, 1922; [*Cent.* 1922, II 574]; not in C.A.; *Ger.* 343,151, Oct. 23, 1921; [*Cent.* 1922, II 143]; not in C.A.; *Brit.* 145,614, June 29, 1920; C.A. 14, 3427 (1920); not in *Cent.*; *Brit.* 155,575/6, Jan. 13, 1921; *Cent.* 1921, II 601; C.A. 15, 1535 (1921); *French* 519,129, June 4, 1921; *Cent.* 1921, IV 803; not in C.A. (127) Kolshorn, *Ger.* 343,994, Nov. 12, 1921; *Cent.* 1922, II 604; not in C.A. (128) Bergmann, Ulpts, Camacho, *Ber.* 55, 2807-2809 (1922). (129) Alquist, Slagh (to Dow Chem. Co.), U.S. 2,147,226, Feb. 14, 1939; *Cent.* 1939, II 526; C.A. 33, 3818 (1939). (130) L. Knorr, E. Knorr, *Ber.* 32, 756-757 (1899).

(131) Roth, *Ber.* 15, 1149-1153 (1882). (132) Rider, Hill, *J. Am. Chem. Soc.* 52, 1528-1530 (1930). (133) Rider, *J. Am. Chem. Soc.* 52, 2115-2118 (1930); U.S. 2,004,132, June 11, 1935; *Cent.* 1935, II 3545; C.A. 29, 4902 (1935). (134) Magidson, Strukow, *Arch. Pharm.* 271, 576-577 (1933). (135) Einhorn, Fiedler, Ladisch, Uhlfelder, *Ann.* 371, 158-161 (1910). (136) Pyman, *J. Chem. Soc.* 93, 1795 (1908). (137) Rider, Cook, *J. Am. Chem. Soc.* 59, 1741 (1937). (138) Raasch, Brode, *J. Am. Chem. Soc.* 64, 1112-1113 (1942). (139) Meyer, *Ber.* 2, 186-188 (1869). (140) Schmidt, Hartmann, *Ann.* 337, 102 (1904).

(141) Biententhal, *Ber.* 33, 3500-3506 (1900). (142) du Pont Co., *Brit.* 477,981, Feb. 10, 1938; *Cent.* 1938, II 183; not in C.A. (143) Fromm, Pirk, *Ann.* 442, 143-144 (1925). (144) Fromm, Kapeller-Adler, *Ann.* 467, 253-254 (1923). (145) Gabriel, Ohle, *Ber.* 50, 824 (1917). (146) Hatch, Alexander, *J. Am. Chem. Soc.* 67, 688 (1945).

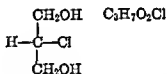
### 3:9039 2-CHLOROPROPANEDIOL-1,3

(Glycerol  $\beta$ -monochlorohydrin,

" $\beta$ -monochlorohydrin,"

$\beta$ -chlorotrimethylene glycol,

$\beta,\beta'$ -dihydroxyisopropyl chloride)



Bell, I - 476

I<sub>1</sub>-(247)

I<sub>2</sub>-(542)

B.P. [146° at 18 mm. (1) (2)]

124.5-125° at 14.6 mm. (3)

124° at 14 mm. (4)

122.5-123.5° at 13.5 mm. (5)

$D_4^{20} = 1.3219$  (4)  $n_D^{20} = 1.4831$  (4)

1.3217 (3)

cf. (4)

$D_4^0 = 1.3416$

1.3375 (3)

Attention is directed to the fact that  $\bar{C}$  is in most respects extremely similar in physical constants and chemical behavior to the isomeric glycerol  $\alpha$ -monochlorohydrin (3-chloropropanediol-1,2) (3:9038); that  $\bar{C}$  is very readily partially isomerized to the latter, and that, therefore, the homogeneity of all preps. of  $\bar{C}$  or reactn. prods. derived from supposedly pure  $\bar{C}$  must be accepted with reserve. The literature of the two glycerol monochlorohydrins is seriously entangled, and reference to the original articles must be made for supporting details.

### PREPARATION OF $\bar{C}$

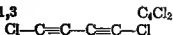
$\bar{C}$  has been isolated (3) from the mixed glycerol monochlorohydrins by fractional hydrolysis and distillation; this isolation has been confirmed (4) (6) by methods based on the slower condensation of  $\bar{C}$  with acetone (see below). — The mixture of glycerol monochlorohydrins obtd. from glycerol (1:6540) with conc. HCl at 120° for 5 hrs. under press. contains (4) 13%  $\bar{C}$ .

- Dubois, *Compt. rend.* 187, 767-769, 949-951 (1928). *Bull. soc. chim.* (4) 47, 570 (1930). (46) den Otter, *Rec. trav. chim.* 57, 18-20 (1938). (47) Banerjee, Sen, *J. Indian Chem. Soc.* 9, 509-518 (1932). (48) Smith, Wode, Widhe, *Z. physik. Chem.* 130, 157-162 (1927). (49) Groll, Hearne (to Shell Development Co.), U.S. 2,086,077, July 6, 1937; *Cent.* 1937, II 2433; *C.A.* 31, 5813 (1937). (50) Bigot, *Ann. chim.* (6) 22, 481-487 (1891). (51) Curme, Young (to Carbide and Carbon Chem. Corp.), Canadian 238,729, March 18, 1924; *Cent.* 1925, I 1129; not in *C.A.* (52) Grün, *Ger.* 272,337, March 27, 1914; *Cent.* 1914, I 1469-1470; *C.A.* 8, 2604 (1914); *Ger.* 227,901, Sept. 3, 1914; *Cent.* 1914, II 812; *C.A.* 9, 1096 (1915). (53) Lourenco, *Ann.* 120, 91 (1861). (54) Koelsch, *J. Am. Chem. Soc.* 52, 1105-1106 (1930). (55) von Richter, *J. prakt. Chem.* (2) 20, 193-195 (1879). (56) Tsunoo, *Ber.* 68, 1342 (1935). (57) Rathsburg, Gawlich, *Chem. Ztg.* 65, 426-427 (1941); *Cent.* 1942, I 651; *C.A.* 37, 3273 (1943). (58) Grün, Boedecker, *Ber.* 43, 1058, Note 1 (1910). (59) Olivier, Berger, *Rec. trav. chim.* 41, 639-640 (1921). (60) Drozdov, Chernov, *J. Gen. Chem. (U.S.S.R.)*, 4, 1305-1309 (1934); *Cent.* 1936, I 4549, *C.A.* 29, 3306 (1935). (61) Smith, *Z. physik. Chem.* 83, 349-352 (1912). (62) Smith, Lindberg, *Ber.* 61, 1709-1717 (1928). (63) Thress, Müller (to M.L.B.), *Ger.* 405,384, Oct. 31, 1924; *Cent.* 1925, I 1527; not in *C.A.* (64) Carius, *Ann.* 124, 222-224 (1862). (65) Nef, *Ann.* 335, 232 (1904). (66) Groll, Hearne (to Shell Development Co.), U.S. 2,070,990, Feb. 16, 1937, *Cent.* 1937, II 2433; *C.A.* 31, 2612 (1937). (67) Marple, Evans (to Shell Development Co.), U.S. 2,248,635, July 8, 1941; *C.A.* 35, 6599 (1941). (68) Nivière, *Bull. soc. chim.* (4) 15, 464-465 (1914). (69) Lüders, (a) *Ger.* 291,541, April 20, 1916; *Cent.* 1916, I 913; *C.A.* 11, 1018 (1917). (b) *Ger.* 291,542, May 15, 1916; *Cent.* 1916, I 1019; *C.A.* 11, 1519 (1917). (70) Lüders, *Emn.* 1915, II 238. (71) Fairbourn, Stephens, 1625 (1920). (72) Bailly, Gaumé, *Compt.* (1924). (73) King, Pyman, *J. Chem. Soc.* 1934, 1233 (1934). (74) Bailly, *Ann. chim.* (9) 6, 127-137 (1916). (75) Oechslein (to Étab Poulenc Frères), *Brit.* 191,028, Feb. 14, 1923; *Cent.* 1923, IV 721, *C.A.* 17, 2887 (1923); *French* 556,366, July 19, 1923; *Cent.* 1923, IV 721, not in *C.A.* (76) Fairbourn, Gibson, Stephens, *J. Soc. Chem. Ind.* 49, 1009 (1930). (77) Smith, Nilsson, *J. prakt. Chem.* (2) 162, 63-70 (1943). (78) Hill, Pyman, *J. Chem. Soc.* 1929, 2236-2238. (79) Groll, Hearne (to Shell Development Co.), U.S. 2,070,990, Feb. 16, 1937, *Cent.* 1937, II 2433; *C.A.* 31, 2612 (1937). (80) Jones, *J. Chem. Soc.* 1933, 167. (81) Romburgh, *Rec. trav. chim.* 1, 156-167 (1882). (82) Smith, *Z. physik. Chem.* 102, 64-65 (1922). (83) Chem Fabrik Griesheim-Elektron, 17; *C.A.* 9, 356 (1915). (84) Nieuwland, 30. (85) Killian, Hennion, Nieuwland, 3370; *C.A.* 20, 1243 (1926). (86) Van Romburgh, *Rec. trav. chim.* 1, 156-167 (1882). (87) Smith, *Z. physik. Chem.* 102, 64-65 (1922).



## 3:9040 1,4-DICHLOROBUTADI-1,3

(Dichlorohiacetylene)



Beil. I —

I<sub>1</sub>—I<sub>2</sub>-(246)

M.P. 1-3° (1)

Long colorless ndls., which can be distilled under N<sub>2</sub> yielding a colorless oil (1). —  $\bar{\text{C}}$  has odor of dichloroacetylene; readily polymerizes to an insol. dark brown explosive material. —  $\bar{\text{C}}$  explodes at 73° (1).

[For prepn. of  $\bar{\text{C}}$  from diacetylene [Beil. I-266] by actn. of alk. hypochlorite soln. in cold and absence of light see (1) (2) (3).]

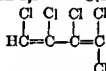
$\bar{\text{C}}$  dislvd. in  $\text{CHCl}_3$  and stood 1 day with I<sub>2</sub> in  $\text{CHCl}_3$  adds 2 moles I<sub>2</sub> yielding (1) 1,4-dichloro-1,2,3,4-tetraiodobutadiene-1,3, which after careful recrystn. from  $\text{C}_6\text{H}_6$ /pet. ether has m.p. 155-157° (1).

3:9040 (1) Straus, Kollek, Hauptmann, *Ber.* 63, 1893-1894 (1930). (2) I.G., Brit. 333,946, Sept. 18, 1930; *Cent.* 1931, I 523. (3) I.G., Ger. 495,787, April 17, 1930.

## 3:9044 1,1,2,3,4-PENTACHLOROBUTADIENE-1,3

C<sub>4</sub>HCl<sub>5</sub>

Beil. I - 250

I<sub>1</sub>—I<sub>2</sub>-(225)

B.P. 125° at 70-80 mm. (1)

[From 2,3,4,5,5-pentachloropentadien-2,4-oic acid-1 [Beil. II-482] by hoilg. with aq., then distilling with steam; the structure of the acid (and therefore of  $\bar{\text{C}}$ ) is disputed (2). — For two other materials (b.p. 193-200° at 720 mm.) having the composition C<sub>4</sub>HCl<sub>5</sub>, obtd. from trichloroethylene (3:5170) with AlCl<sub>3</sub>, hut thought *not* to be identical with  $\bar{\text{C}}$ , see (3).]

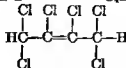
3:9044 (1) Zincke, Kuster, *Ber.* 26, 2113 (1893). (2) Zincke, *Ann.* 296, 143 (1897). (3) Kaufner, *Ann.* 433, 48-51 (1923).

## 3:9046 1,1,2,3,4,4-HEXACHLOROBUTENE-2

(Liquid stereoisomer)

C<sub>4</sub>H<sub>2</sub>Cl<sub>6</sub>

Beil. S.N. 11



B.P. 07-98° at 10 mm. (1)

 $D_{15}^{15} = 1.651$  (1)  $n_D^{20} = 1.53313$  (1)

[See also solid stereoisomer (3:1945).]

Colorless oily liq. with agreeable odor.

[For formn. of  $\bar{\text{C}}$  (together with its solid stereoisomer (3:1945)) by actn. of Cl<sub>2</sub> upon the high-boilg. fraction obtd. in the prepn. of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1); for formn. of  $\bar{\text{C}}$  from the liq. stereoisomer (3:6150) of 1,2,3,4-tetrachlorobutadiene-1,3 + Cl<sub>2</sub> see (1).]

3:9046 (1) Müller, Hüther, *Ber.* 64, 589-600 (1931); *C.A.* 25, 3956-3957 (1931).

[For formn. of  $\bar{C}$  (together with the isomeric  $\alpha$ -monochlorohydrin) from a mixt. of monochlorohydrin diacetates with abs. MeOH contg. dry HCl gas see (7).]

[The mixture of the two glycerol monochlorohydrins obt'd. from allyl alcohol (1:6145) by addn. of HOCl (1) (8) (5) cf. (6) (9) (10) (11) (13) or from epichlorohydrin (3:5358) q.v. by addn. of aq. in pres. of acids has been shown (12) to be essentially similar to that obt'd. from glycerol with HCl, although different proportions of  $\alpha$ - and  $\beta$ - isomers might be anticipated (3).]

### CHEMICAL BEHAVIOR OF $\bar{C}$

Reduction of  $\bar{C}$ . [ $\bar{C}$  with Na/Hg in aq. alc. HCl gives (8) trimethylene glycol (1:6490).]

Behavior with aq. alkalis. [ $\bar{C}$  with aq. alk. loses HCl and ring-closes to 3-hydroxy-1,2-epoxypropane (glycidol = epihydrin alcohol): this reactn. occurs with  $\bar{C}$  very much more slowly than for the isomeric  $\alpha$ -monochlorohydrin (3:9038); for its use in detn. of purity of  $\bar{C}$  see (6) (3) (13) (14).]

Behavior with alkali cyanides. [ $\bar{C}$  in 95% alc. with aq. KCN (or NaCN) in s.t. at 100° for 36 hrs., followed by hydrolysis, does *not* (6) give the expected  $\beta,\beta'$ -dihydroxyisobutyric acid but instead gives (35% yield (6)) the lactone of  $\beta,\gamma$ -dihydroxy-*n*-butyric acid ( $\beta$ -hydroxy-*n*-butyro- $\gamma$ -lactone), m.p. 22.5–26° (6), i.e., the same prod. similarly obt'd. from glycerol  $\alpha$ -monochlorohydrin (3:9038).]

Behavior with NaI. [ $\bar{C}$  with dry NaI in anhydrous acetone in s.t. at 100° for 12 hrs. gives (18% yield (15)) glycerol  $\beta$ -mono-iodohydrin, m.p. 52–53° (15).]

Behavior with acetone. [ $\bar{C}$  in acetone with  $P_2O_5$  at 2–7° gives (57% yield (4)) a condensation prod., "acetone- $\beta$ -chlorohydrin,"  $C_6H_{11}O_2Cl$ , h.p. 161.5–162.2° cor. at 757 mm.,  $D_4^{25} = 1.1344$ ,  $n_D^{25} = 1.4487$ , this condensation occurs less readily, however, than the analogous reactn. for glycerol  $\alpha$ -monochlorohydrin (3:9038), and removal of the latter by this means has been used (4) to enrich the proportion of  $\bar{C}$  in a mixt. of the two.]

— Glycerol  $\beta$ -monochlorohydrin  $\alpha$ -acetate: oil, b.p. 230° at 760 mm., 230–234° cor. at 750 mm. (10),  $D_4^{25} = 1.235$  (10). (See 3:6648.)

— Glycerol  $\beta$ -monochlorohydrin  $\alpha,\alpha'$ -diacetate: oil, h.p. 101–102° at 4 mm. (15).

— Glycerol  $\beta$ -monochlorohydrin  $\alpha$ -benzoate: unreported.

— Glycerol  $\beta$ -monochlorohydrin  $\alpha,\alpha'$ -dibenzoate: oil, h.p. 210–211° at 1.5 mm. (15).

— Glycerol  $\beta$ -monochlorohydrin  $\alpha,\alpha'$ -bis-(*p*-nitrobenzoate): m.p. 121–122° (16) (7).

[Prepd. indirectly; note that this prod. depresses the m.p. of authentic glycerol  $\alpha$ -monochlorohydrin bis-(*p*-nitrobenzoate), m.p. 108–109° u.c. (7).]

— Glycerol  $\beta$ -monochlorohydrin  $\alpha$ -(*N*-phenylcarbamate): m.p. 133–136° (6), 131–133° remelting at 133° (12). [From  $\bar{C}$  with phenyl isocyanate in 6% yield (6); note that, for the corresp. deriv. of glycerol  $\alpha$ -monochlorohydrin, m.p. is 128–129° (12).]

3:9039 (1) Hanriot, *Ann. chim.* (5) 17, 73–75, 76–78 (1870). (2) Chabon, *J. Soc. Chim. Paris*, 949–950 (1931). (3) Smith, *Z. physik. Chem.* 94, 723–7; 509–516 (1931). (4) Read, Hurst, *J. Chem. Soc.* 121, Spieth, Hutton, *J. Am. Chem. Soc.* 53, 3169–3171 (1931). (5) Henry, *Ber.* 5, 449 (1872); *Bull. acad. roy. Belg.* (3) 23, 110–114; *Cent.* 1897, I 741. (6) Essex, Ward (to du Pont Co.), U.S. 1,594,608, Aug. 3, 1926; *Cent.* 1926, II 1693; *C.A.* 20, 3170–3171 (1926). (10) Wegscheider, Zmierzlikar, *Monatsh.* 34, 1071–1072 (1913).

07 (1943).  
Chem. 92,  
133, *J. Am.*

$\bar{C}$  is volatile with steam (use in sepn. from accompanying resin (1)).

$\bar{C}$  reduces Tollens' soln. but not  $\text{NH}_4\text{OH}/\text{AgNO}_3$  without alkali (1).

$\bar{C}$  is not attacked by boilg. 0.1%  $\text{KMnO}_4$  (1).

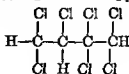
$\bar{C}$  on boilg. with excess  $N/10$  alc.  $\text{KOH}$  splits off 2.34-2.6 moles  $\text{HCl}$  but  $\bar{C}$  cannot be titrated (1).

3:9054 (1) *Prins, Rec. trav. chim.* 56, 123-124 (1937).

### 3:9056 1,1,2,2,3,4,4-HEPTACHLOROBUTANE

 $\text{C}_4\text{H}_3\text{Cl}_7$ 

Beil. S.N. 10



B.P. 137.5° at 13.5 mm. (1)

$D_{20}^{20} = 1.742$  (1)

$n_D^{20} = 1.5407$  (1)

97.5° at 2 mm. (1)

[For prepn. of  $\bar{C}$  (60% yield (1) together with other products) from 1,2-dichloroethylene (3:5030) + pentachloroethane (3:5880) +  $\text{AlCl}_3$  for 12 days at 40° see (1).]

$\bar{C}$  in  $\text{CCl}_4$  gives with  $\text{AlCl}_3$  a yel. color; no  $\text{HCl}$  is evolved on boilg., and on addn. of water the solution is completely decolorized (1).

$\bar{C}$  with  $\text{Zn}$  dust in alc. gives (50% yield (1)) of a trichlorobutadiene, b.p. 161°, 52° at 12 mm. (1).

3:9056 (1) *Prins, Rec. trav. chim.* 56, 124-125 (1937).

### 3:9057 1,2-DICHLOROBUTADIENE-1,3

 $\text{Cl} \quad \text{Cl}$ 
 $\text{C}_4\text{H}_4\text{Cl}_2$ 

Beil. S.N. 12



B.P. 60-65° at 105 mm. (4)

$D_{15}^{15} = 1.207$  (1)

$n_D^{15} = 1.5078$  (1) (5)

46.75-47.5° at 85 mm. (5)

60-65° at 40 mm. (1)

$D_4^{15} = 1.199$  (5)

$n_D^{15} = 1.4698$  (2)

$\bar{C}$  polymerizes slower than chloroprene (3:7080) yielding a rubberlike polymer which on vulcanization gives an ebonite-like subst. (1).

[For prepn. of  $\bar{C}$  (56% yield (4)) from 1-chloro-2-vinylacetylene (3:7070) by treatment as directed at room temp. with conc.  $\text{HCl}$  +  $\text{CuCl}$  +  $\text{NH}_4\text{Cl}$  see (4); for formn. from vinylacetylene +  $\text{Cl}_2$  see (3); for prepn. of  $\bar{C}$  from 1,2,4-trichlorobutene-2 (3:9062) with  $\text{EtOH}/\text{KOH}$  see (5).]

$\bar{C}$  on oxidn. with  $\text{KMnO}_4$  yields (3) oxalic acid dihydrate (1:0445). —  $\bar{C}$  on ozonization in  $\text{CCl}_4$  (3) yields oxalic acid (1:0535) and formic acid (1:1005); under specified conditions, however,  $\alpha,\beta$ -dichloroacrylic acid (3:2265), m.p. 85-86°, has been isolated (3).

$\bar{C}$  fails to add maleic anhydride (3). — [For behavior of  $\bar{C}$  with  $\text{HOBr}$  or with  $\text{HgO}$  +  $\text{I}_2$  +  $\text{MeOH}$  see (6).]

R. 1935, No. 2, 189-226;  
(1936). (2) Klebanski,  
nt. 1936, 1 3414; C.A. 30,  
nt. 389,122, April 4, 1933;  
56 (1043); C.A. 38, 1467  
38, 329-330 (1944).

3:0048 HEXACHLOROBUTENE-X  $C_4H_2Cl_6$  Beil. S.N. 11

B.P. 106-107.5° at 14 mm. (1)

[For formn. of  $\bar{C}$  from 1,1,2,2,3,4,4-heptachlorobutane (3:9056) with conc. aq. KOH see (1).]

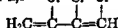
 $\bar{C}$  reduces Tollens' reagt. (1).3:9048 (1) Prins, *Rec. trav. chim.* 56, 125 (1937); *Cent.* 1937, I 3308; *C.A.* 31, 2999 (1937).3:9050 HEXACHLOROBUTENE-Y  $C_4H_2Cl_6$  Beil. S.N. 11

B.P. M.P.  
125.5° at 25 mm. (1) 9.5-11° (1)  $D_4^{20} = 1.6880$  (1)  $n_D^{20} = 1.5442$  (1)

[For formn. of  $\bar{C}$  (together with other products) by actn. of  $F_2$  on trichloroethylene (3:5170) see (1).]

 $\bar{C}$  does not add  $Cl_2$  or  $Br_2$  in sunlight (1).

$\bar{C}$  differs (1) in prop. from the solid stereoisomer (3:1945) of 1,1,2,3,4,4-hexachlorobutene-2.

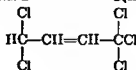
3:9050 (1) Miller, *J. Am. Chem. Soc.* 62, 343 (1940).3:9052 1,2,3-TRICHLOROBUTADIENE-1,3  $C_4H_3Cl_3$  Beil. S.N. 12

B.P. 33-34° at 7 mm. (1) (2)  $D_4^{20} = 1.4060$  (1)  $n_D^{20} = 1.5262$  (1)

[For prepn. of  $\bar{C}$  from 1,2,2,3,4-pentachlorobutane (3:9070) (55% yield of  $\bar{C}$  together with 25% yield 2,3,3,4-tetrachlorobutene-1 (3:9060)) with alc. KOH for 2 hrs. at room temp. see (1) (2).]

$\bar{C}$  after addition of hydroquinone can be distd. in vac. (1). —  $\bar{C}$  polymerizes more slowly than 2,3-dichlorobutadiene-1,3 (3:5220); under ordinary conditions  $\bar{C}$  changes in 10-12 days to a jelly-like mass contg. 50% unchanged  $\bar{C}$ , after a month polymerization to a dark-colored soft friable mass is apparently complete (1).

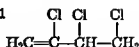
3:9052 (1) Carothers, Berchet, *J. Am. Chem. Soc.* 55, 2004-2008 (1933) (2) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1931, *Cent.* 1935, I 3724; *C.A.* 28, 5716 (1934).

3:0054 1,1,1,4,4-PENTACHLOROBUTENE-2  $C_4H_3Cl_5$  Beil. S.N. 11

B.P. 78.5-80° at 11 mm. (1)  $D_{11}^{22} = 1.011$  (1)  $n_D^{22} = 1.5518$  (1)  
76-77.0° at 10 mm. (1)  $D_{11}^{21} = 1.612$  (1)  $n_D^{21} = 1.5538$  (1)

[For prepn. of  $\bar{C}$  (in small yield and with much resinification (1)) from either trichloroethylene (3:5170) + 1,1,2-trichloroethane (3:5330) +  $AlCl_3$  for 7 days at 40°, or from 1,2-dichloroethylene (3:5030) + 1,1,1,2-tetrachloroethane (3:5555) +  $AlCl_3$  for 10 days at 40°, see (1).]

3:9064 2,3,4-TRICHLOROBUTENE-1  
(1,2,3-Trichlorobutene-3)



$\text{C}_4\text{H}_5\text{Cl}_3$  Beil. S.N. 11

B.P. 40-41° at 10 mm. (1)

$D_4^{20} = 1.3430$  (1)  $n_D^{20} = 1.4944$  (1)

37-41° at 10 mm. (2)

36-40° at 6 mm. (2)

[For formn. of  $\bar{\text{C}}$  from 4-chlorohutadiene-1,2 (3:7225) (together with 1,2,4-trichlorobutene-2 (3:9062)) especially at low temps., e.g., -60 to -70°, see (1). Note that at 40-60°  $\bar{\text{C}}$  formed by this reactn. reacts further with the hy-product 1,2,4-trichlorobutene-2 (3:9062) to yield (1) as the principal product 1,2,3,3-tetrachlorobutane (3:9080) q.v.; for formn. of  $\bar{\text{C}}$  from 2-chlorohutadiene-1,3 (Chloroprene) (3:7080) with  $\text{Cl}_2$  see (2) (3).]

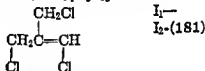
$\bar{\text{C}}$  with alk. as specified (2) gives 2,3-dichlorohutadiene-1,3 (3:5220), h.p. 98° at 760 mm. (2).

$\bar{\text{C}}$  on htg. with 2 pts. aq. + calcd. amt. powdered  $\text{CaCO}_3$  for 4 hrs. at 70° fails (4) to hydrolyze [diff. from 1,2-dichlorobutene-2 (3:5615) or 1,3-dichlorobutene-2 (3:5550)]. —  $\bar{\text{C}}$  does react, however, with hot aq.  $\text{K}_2\text{CO}_3$  losing  $\text{HCl}$  and yielding (4) alm. 100% 2,3-dichlorohutadiene-1,3 polymer (4).

$\bar{\text{C}}$  on oxidn. with aq.  $\text{KMnO}_4$  yields (1)  $\alpha,\beta$ -dichloropropionic acid, (3:0855), m.p. 49-50°, Neut. Eq. 141 (calcd. 143) (1).

3:9064 (1) Carothers, Berchet, *J. Am. Chem. Soc.* 55, 1628-1631 (1933). (2) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3  
(to du Pont), U.S. 1,964,720, July  
chenko, *J. Gen. Chem. (U.S.S.R.)*

3:9066 1,3-DICHLORO-2-(CHLOROMETHYL)PROPENE-1  $\text{C}_4\text{H}_5\text{Cl}_3$  Beil. I —



B.P. 62-64° at 9 mm. (1) (2)

[For formn. of  $\bar{\text{C}}$  (together with other products) from 1,3-dichloro-2-chloromethyl-2-nitropropane [Beil.  $\text{I}_2$ -(92)] with  $\text{Na}/\text{Hg}$  (2) or from 2-nitro-2-hydroxymethylpropanediol-1,3 [Beil.  $\text{I}_2$ -(596)] with  $\text{PCl}_5$  (1) see (1) (2).]

$\bar{\text{C}}$  on cat. hydrogenation with Pt black in alc. yields (2) 1,3-dichloro-2-methylpropane (3:7960), h.p. 45° at 10 mm.

$\bar{\text{C}}$  in  $\text{CHCl}_3$  on shaking with  $\text{Cl}_2$ /aq. adds  $\text{Cl}_2$  yielding (2) 1,1,2,3-tetrachloro-2-chloromethylpropane (3:9072), h.p. 99-101° at 12 mm. —  $\bar{\text{C}}$  with  $\text{Br}_2$  in  $\text{CHCl}_3$  adds  $\text{Br}_2$  yielding (2) 1,2-dibromo-1,3-dichloro-2-(chloromethyl)propane, colorless odorless oil, h.p. 140° at 10 mm.

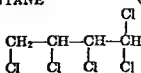
[For reactn. of  $\bar{\text{C}}$  with sodio-malonic ester see (3).]

3:9066 (1) Kleinfeller, *Ber.* 62, 1585-1587 (1929). (2) Kleinfeller, *Ber.* 62, 1594-1595 (1929).  
(3) Kleinfeller, Frercks, *J. prakt. Chem.* (2) 138, 195-196 (1933).

3:9068 1,1,2,3,4-PENTACHLOROBUTANE

(Liquid diastereoisomer)

(1,2,3,4,4-Pentachlorobutane  
(liquid diastereoisomer))

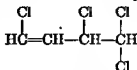


$\text{C}_4\text{H}_5\text{Cl}_5$  Beil. S.N. 10

B.P. 95.3-95.5° at 11 mm. (1)

[See also solid diastereoisomer (3:0750).]

3:9058 1,3,4,4-TETRACHLOROBUTENE-1  $C_4H_4Cl_4$  Beil. S.N. 11  
(1,1,2,4-Tetrachlorobutene-3)

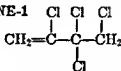


B.P. 82-83° at 17 mm. (1)

[For prepn. of  $\bar{C}$  from 1,2-dichloroethylene (3:5030) by polymerization in pres. of peroxide cat. see (1).]

3:9058 (1) Baucr, U.S. 2,267,712, Dec. 30, 1941; C.A. 36, 2564 (1942).

3:9060 2,3,3,4-TETRACHLOROBUTENE-1  $C_4H_4Cl_4$  Beil. S.N. 11  
(1,2,2,3-Tetrachlorobutene-3)



B.P. 41-42° at 7 mm. (1)

$D_4^{20} = 1.4602$  (1)  $n_D^{20} = 1.5133$  (1)

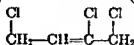
[For formn. of  $\bar{C}$  (25% yield (1)) from 1,2,3,3,4-pentachlorobutane (3:9070) with MeOH/KOH at room temp. for 2 hrs. (together with 55% yield 1,2,3-trichlorobutadiene-1,3 (3:9052)) see (1).]

$\bar{C}$  on oxidn. with excess aq.  $KMnO_4$  yields (1)  $\alpha,\alpha,\beta$ -trichloropropionic acid (3:1275), m.p. 48-50°, Neut. Eq. 176.4 (calcd. 177.5) (1).

[A liquid, b.p. 90-110° at 25 mm.,  $D_4^{21} = 1.473$ ,  $n_D^{21} = 1.514$ , and believed to be a mixt. of tetrachlorobutenes, has been obtd. (2) from monovinylacetylene +  $Cl_2$ ; it may or may not have contained  $\bar{C}$ .]

3:9060 (1) Berchet, Carothers, J. Am. Chem. Soc. 55, 2004-2008 (1933). (2) Rengert, Schumacher, Ber. 73, 1025-1042 (1940); C.A. 35, 1027 (1941).

3:9062 1,2,4-TRICHLOROBUTENE-2  $C_4H_3Cl_3$  Beil. S.N. 11  
(1,3,4-Trichlorobutene-2)



B.P. 67-60° at 10 mm. (3)

$D_4^{20} = 1.3843$  (1)  $n_D^{20} = 1.5175$  (1)

61-65° at 10 mm. (1)

62-65° at 11 mm. (2)

$D_4^{15} = 1.3575$  (3)  $n_D^{15} = 1.5121$  (3)

[For formn. of  $\bar{C}$  from 4-chlorobutadiene-1,2 (3:7225) +  $Cl_2$  (together with 2,3,4-trichlorobutene-1 (3:9061) and 1,2,2,3,4-pentachlorobutane) see (1) (2); for formn. of  $\bar{C}$  from 2-chlorobutadiene-1,3 (Chloroprene) (3:7050) +  $Cl_2$  (together with 2,3,4-trichlorobutene-1 (3:9061) and 1,2,2,3,4-pentachlorobutane (3:9070)) see (1) (2) (3).]

$\bar{C}$  with NaOH/KOH as directed (3) loses HCl giving 1,2-dichlorobutadiene-1,3 (3:9057).

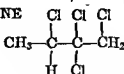
$\bar{C}$  on oxidn. with aq.  $KMnO_4$  yields (1) (3) chloroacetic acid (3:1370), m.p. 63°, Neut. Eq. 95.1 (calcd. 94.5) (1).

3:9062 (1) Carothers, Berchet, J. Am. Chem. Soc. 55, 1629-1631 (1933). (2) Carothers, Berchet (du Pont), U.S. 1,965,369, July 3, 1934; Cent. 1935, 1 3724; C.A. 28, 5716 (1934). (3) Petrov, J. Gen. Chem. (U.S.S.R.) 13, 102-107 (1943); C.A. 33, 329 (1944).

[For prepn. of  $\bar{C}$  in 55% yield (1) from 2-chlorobutene-2 (3:7105) by treatment with 1 mole  $Cl_2$  + 1.5 moles  $NaHCO_3$  at  $0^\circ$  (accompanied by 45% yield 2,2,3-trichlorobutane (3:5680)) see (1); with  $Cl_2$  in pres. of light and  $O_2$  as directed see (2).]

3:9074 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, II 4223; *C.A.* 33, 4190 (1939). (2) Hearne (to Shell Development Co.), U.S. 2,296,614, Sept. 22, 1942; *C.A.* 37, 1129 (1943).

3:9078 1,2,2,3-TETRACHLOROBUTANE  $C_4H_2Cl_4$  Beil. I-119



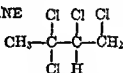
B.P. 63.0-63.5° at 11 mm. (1)  $D_4^{18} = 1.4276$  (1)  $n_D^{18} = 1.4893$  (1)

[For prepn. (100% yield (1)) from 1,2-dichlorobutene-2 (3:5615) with 1 mole  $Cl_2$  + 1.5 moles  $NaHCO_3$  at  $0^\circ$  see (1).]

[The product obtained (2) cf. (3) from 2,2,3-trichlorobutanol-1 (3:1336) with  $PCl_5$  may have been impure  $\bar{C}$ .]

3:9078 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *C.A.* 33, 4190 (1939). (2) Garzarolli-Thurnlaekh, *Ann.* 213, 372-373 (1882). (3) Norton, Noyes, *Am. Chem. J.* 10, 432 (1888).

3:9080 1,2,3,3-TETRACHLOROBUTANE  $C_4H_2Cl_4$  Beil. S.N. 10

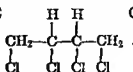


B.P. 90° at 32 mm. (1)  $D_4^{20} = 1.4204$  (1)  $n_D^{20} = 1.4958$  (1)  
55-57° at 10 mm. (1)

[For formn. of  $\bar{C}$  (together with other products) from 1,3-dichlorobutene-2 (3:5550) at 40-60° with  $Cl_2$  see (1). Note, however, that at very low temps. (-60 to -70°) much  $HCl$  is evolved during chlorination and the principal products are then 2,3,4-trichlorobutene-1 (3:9064), b.p. 40-41° at 10 mm. (1), and 1,2,3,3,4-pentachlorobutane (3:9070), b.p. 85° at 10 mm. (1).] [For patents on this process see (2) (3).]

3:9080 (1) Carothers, Berchet, *J. Am. Chem. Soc.* 55, 1629-1631 (1933). (2) Coffman (to du Pont), U.S. 1,964,720, July 3, 1934; *Cent.* 1934, II 3180; *C.A.* 28, 5080 (1934). (3) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934; *Cent.* 1935, I 3724; *C.A.* 28, 5716 (1934).

1,2,3,4-TETRACHLOROBUTANE  
(Solid isomer)



$C_4H_2Cl_4$  Beil. I-119  
I<sub>1</sub>- (38)  
I<sub>2</sub>-

B.P. 130-134° at 40 mm.

M.P. 73°

See 3:1760. Division A: Solids.

[For prepn. of  $\bar{C}$  (30-50% yield of mixed solid and liquid stereomers (1)) from 1,2-dichloroethylene (3:5030) + 1,1,2-trichloroethane (3:5330) + 1%  $AlCl_3$  for 5 days at 35-40° see (1).]

$\bar{C}$  in  $CCl_4$  treated with  $AlCl_3$  gives a dark violet soln. which on boilg. evolves  $HCl$  (1).

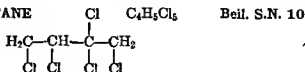
$\bar{C}$  in alc. treated with  $Zn$  dust gives (60% yield (1)) 1-chlorobutadiene-1,3 (3:7210), b.p. 68° (1).

$\bar{C}$  dissolved in hot alc. and titrated with  $N/10$   $KOH$  splits off 1.51-1.59 moles  $HCl$  (1).

[A pentachlorobutane obtained (2) from trichloroethylene (3:5170) + 1,1-dichloroethane (3:5035) +  $AlCl_3$  may or may not be identical with  $\bar{C}$ .]

3:9068 (1) *Prins. Rec. trav. chim.* 56, 121-123 (1937). (2) Consortium fur Elektrochem. Ind., Brit. 453,414, Oct. 8, 1936, *Cent.* 1937, I 1012.

3:9070 1,2,2,3,4-PENTACHLOROBUTANE  
(1,2,3,3,4-Pentachlorobutane)



B.P. 85° at 10 mm. (1)

$D_4^{20} = 1.5543$  (1)  $n_D^{20} = 1.5157$  (1)

78-84° at 9 mm. (2)

82-86° at 6 mm. (2)

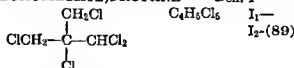
[For prepn. of  $\bar{C}$  from 1,3-dichlorobutene-2 (3:5550) by actn. of  $Cl_2$  at low temps. (-60 to -70°), much  $HCl$  being evolved and 2,3,4-trichlorobutene-1 (3:9064) also being formed, see (1); note also that chlorination of 4-chlorobutadiene-1,2 (3:7225) gives mixts. of 2,3,4-trichlorobutene-1 (3:9064) and 1,2,4-trichlorobutene-2 (3:9062) which react further to yield  $\bar{C}$  (1).] [For patents on these processes see (2) (3).]

$\bar{C}$  with alk. yields (2) both 1,2,3-trichlorobutadiene-1,3 (3:9052), b.p. 34° at 7 mm. (2), and 2,3,3,4-tetrachlorobutene-1 (3:9060), b.p. 42° at 7 mm. (2).

3:9070 (1) Carothers, Berchet, *J. Am. Chem. Soc.* 55, 1628-1631 (1933). (2) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934; *Cent.* 1935, I 3724; *C.A.* 28, 5716 (1934). (3) Coffmann (to du Pont), U.S. 1,964,720, July 3, 1934; *Cent.* 1934, II 3180; *C.A.* 28, 5080 (1934).

3:9072 1,1,2,3-TETRACHLORO-2-(CHLOROMETHYL)PROPANE

Beil. I —

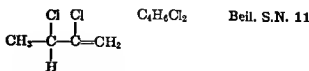


B.P. 99-101° at 12 mm. (1)

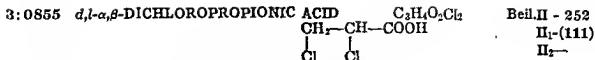
[For prepn. of  $\bar{C}$  from 1,3-dichloro-2-(chloromethyl)propene-1 (3:9066) by shaking in  $CHCl_3$  with  $Cl_2$ /aq. see (1)]

3:9072 (1) Kleinfeller, *Ber.* 62, 1595 (1929).

3:9074 2,3-DICHLOROBUTENE-1







M.P. 50° (1) (10) B.P. 210° sl. dec. at 762 mm. (1)  
 49.5° (2) 130-133° at 26 mm. (3)  
 49-50° (3) 112-115° at 12 mm. (5)  
 49° (4)  
 47-50° (5)

[For prepn. from methyl  $\alpha,\beta$ -dichloropropionate (3:9103) by boilg. with 20% HCl (65% yield) see (3); from 2,3-dichloropropanol-1 ("β-dichlorohydrin") (3:6060) by oxidn. with HNO<sub>3</sub> see (1) (6) (7) (2) (5); from  $\alpha,\beta$ -dichloroacrolein by oxidn. with HNO<sub>3</sub> see (7); from  $\alpha$ -chloropropionic acid (3:6125) with Cl<sub>2</sub> at 45° see (8); for formn. of  $\bar{\text{C}}$  from  $\alpha$ -chloroacrylic acid (3:1445) (6) (9) or from  $\alpha$ -chloro-β-hydroxypropionic acid ( $\alpha$ -chlorohydracrylic acid) [Beil. III-298] (10), or  $\alpha,\beta$ -dihydroxypropionic acid (glyceric acid) (11) by htg. with fung. HCl in a.t. at 100°, see indic. refs.]

$\bar{\text{C}}$  with aq. or alc. readily loses HCl yielding (12) (6) (9)  $\alpha$ -chloroacrylic acid (3:1445), m.p. 65°.

$\bar{\text{C}}$  in MeOH treated as directed (13) with activated Zn gives (72% yield) acrylic acid (1:1020), b.p. 140°.

[ $\bar{\text{C}}$  with SOCl<sub>2</sub> gives (15)  $\alpha,\beta$ -dichloropropionyl chloride (3:0032).]

$\bar{\text{C}}$  htd. with Ag<sub>2</sub>CO<sub>3</sub> yields (5)  $\alpha$ -chloro-β-hydroxypropionic acid ( $\alpha$ -chlorohydracrylic acid).

— Methyl  $\alpha,\beta$ -dichloropropionate: b.p. 72-75° at 21 mm. (see 3:0103).

— Ethyl  $\alpha,\beta$ -dichloropropionate: b.p. 183-184° (see 3:6090). [For the *sec*-butyl,  $\beta$ -chloroethyl, and cyclohexyl esters of  $\bar{\text{C}}$  see (3); for glycol and other esters see (14).]

—  $\alpha,\beta$ -Dichloropropionamide: unreported.

—  $\alpha,\beta$ -Dichloropropionanilide: unreported.

—  $\alpha,\beta$ -Dichloropropion-*p*-toluidide: unreported.

3:0855 (1) Henry, *Ber.* 7, 414 (1874). (2) Bockemüller, Hoffmann, *Ann.* 519, 190 (1935). (3) Marvel, Dec, Cooke, Cowan, *J. Am. Chem. Soc.* 62, 3495-3498 (1940). (4) Simpson, *J. Am. Chem. Soc.* 40, 676, 679 (1918). (5) Koelsch, *J. Am. Chem. Soc.* 52, 3385 (1930). (6) Werigo, Melikov, *Ber.* 10, 1499-1500 (1877). (7) Yarnall, Wallis, *J. Org. Chem.* 4, 287 (1939). (8) Röhm & Haas Co., Ger. 579,654, June 29, 1931; *Cent.* 1933, II 1587. (9) Otto, Beckurts, *Ber.* 18, 244 (1885). (10) Melikov, *Ber.* 13, 274 (1880).

(11) Werigo, Melikov, *Ber.* 12, 178 (1879). (12) Werigo, Werner, *Ann.* 170, 168 (1873). (13) Röhm & Haas Co., Ger. 575,423, Apr. 27, 1933; *Cent.* 1933, II 133. (14) Pollack (to Pittsburgh Plate Glass Co.), U.S. 2,257,021, Sept. 23, 1941; *C.A.* 36, 95-96 (1942). (15) Leimu, *Ber.* 70, 1046, 1050 (1937).

3:9082

1,2,3,4-TETRACHLOROBUTANE (liquid isomer)  $\cdot$   $C_4H_6Cl_4$  Beil. I - 119

(Butadiene tetrachloride (liquid isomer);  $CH_2-CH-CH-CH_2$  I<sub>1</sub>-( 38)

(erythrene tetrachloride (liquid isomer))  $\begin{array}{cccc} & Cl & Cl & Cl & Cl \\ & | & | & | & | \end{array}$  I<sub>2</sub>—

B.P. 110–111° at 40 mm. (1) (2)

For formn. and reactns. see solid form, m.p. 73° (3:1760).

3:9083 (1) Muskat, Northrup, *J. Am. Chem. Soc.* 52, 4053–4055 (1930). (2) Muskat (to du Pont), U.S. 2,038,593, Apr. 28, 1936; *Cent.* 1936, II 3359; *C.A.* 30, 3912 (1936).

3:9084

1,1,3-TRICHLORO-2-(CHLOROMETHYL)PROPANE  $C_4H_6Cl_4$  Beil. I —

$\begin{array}{c} CH_2Cl \\ | \\ ClCH_2-C-CHCl_2 \\ | \\ H \end{array}$  I<sub>1</sub>—  
I<sub>2</sub>-(89)

B.P. 77–80° at 9 mm. (1)

Oil with odor like  $CCl_4$  but with irritating actn. on eyes. — Volatile with steam.  
[For formn. of  $\bar{C}$  in small amt. (together with other products) from 2-nitro-2-hydroxy-methylpropanediol-1,3 (nitro-isobutylglycerol) with  $PCl_5$  see (1).]

3:9084 (1) Kleinfeller, *Ber.* 62, 1585 (1929).

3:9080

1,1,3-TRICHLOROBUTANE  $C_4H_7Cl_3$  Beil. S.N. 10

$\begin{array}{c} Cl \\ | \\ CH_3-C-CH_2CHCl_2 \\ | \\ H \end{array}$

B.P. 150° at 720 mm. (1)

A trichlorobutane which may have this structure has been reported (1) when vinyl chloride (3:7004) +  $AlCl_3$  at 20° reacts with the material obtd from ethylidene dichloride (3:5035) +  $AlCl_3$  + chlorinated ethylenes.

3:9086 (1) Consortium für Elektrochem. Ind., Brit. 453,414, Sept. 10, 1936; *Cent.* 1937, I 1012; *C.A.* 31, 1046 (1937).

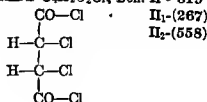
—

$d,l$ - $\alpha,\alpha'$ -DICHLOROSUCCINYL (DI)CHLORIDE  $C_4H_2O_2Cl_4$  Beil. II —

$\begin{array}{c} CO-Cl \\ | \\ H-C-Cl \\ | \\ Cl-C-H \\ | \\ CO-Cl \end{array}$  II<sub>1</sub>—  
II<sub>2</sub>-(558)

B.P. 78.5° at 7 mm. M.P. 39°

See 3:0395. Division A: Solids.

3:9087 *meso*- $\alpha,\alpha'$ -DICHLOROSUCCINYL(DI)CHLORIDE  $C_4H_2O_2Cl_4$  Beil. II - 619

B.P. 105-106° at 45 mm. (1)

85-86° at 22 mm. (1)

79-80° at 15 mm. (2)

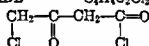
Colorless viscous lachrymatory oil.

[For prepn. of  $\bar{C}$  from fumaryl (di)chloride (3:5875) in  $CCl_4$  soln. with  $Cl_2$  in direct sunlight (100% yield (3)) (1) (2) see indic. refs.]

$\bar{C}$  with aq. reacts only very slowly on mere standing (1), but on continuous shaking with cooling readily hydrolyzes yielding (1) (2) *meso*- $\alpha,\alpha'$ -dichlorosuccinic acid (3:4930).

[ $\bar{C}$  with  $C_6H_6 + AlCl_3$  gives (60% yield (3)) *meso*-1,2-dichloro-1,2-dihenzoylthane (*meso*-2,3-dichloro-1,4-diphenylbutandione-1,4), m.p. 167° (4) (5), accompanied under certain conditions (3) by some  $\alpha,\beta$ -dichloro- $\gamma,\gamma$ -diphenylbutyrolacetone, m.p. 141-142° (3), presumably arising from reactn. of  $\bar{C}$  in the unsymmetrical (phthalide type) form.]

3:9087 (1) Michael, Tissot, *J. prakt. Chem.* (2) 46, 394-395 (1892). (2) Holmberg, *J. prakt. Chem.* (2) 84, 148 (1911). (3) Lutz, *J. Am. Chem. Soc.* 49, 1109-1110 (1927). (4) Conant, Lutz, *J. Am. Chem. Soc.* 47, 885-886 (1925). (5) Lutz, *J. Am. Chem. Soc.* 48, 2908, 2911 (1926).

3:9088  $\gamma$ -CHLOROACETOACETYL CHLORIDE  $C_4H_4O_2Cl_2$  Beil. III -( $\gamma$ -Chloro- $\beta$ -keto-*n*-butyryl chloride)III<sub>1</sub>-  
III<sub>2</sub>-

B.P. 117-119° at 17 mm. (1)

93-96° at 8 mm. (1)

 $D_4^{20} = 1.4397$  (1)  $n_D^{20} = 1.4860$  (1)

Orange-colored liq. which fumes in air.

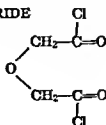
[For prepn. of  $\bar{C}$  from acetylketene (ketene dimer) (2) (3) with  $Cl_2$  in cold  $CCl_4$  soln. see (1).]

$\bar{C}$  with aq. yields chloroacetone (3:5425) +  $CO_2$  +  $HCl$  (note that this method gives chloroacetone free from higher chlorination products (3)).

[ $\bar{C}$  with excess abs.  $EtOH$  at 0° gives (1) (3) ethyl  $\gamma$ -chloroacetoacetate (3:6375).]

$\bar{C}$  with aniline in  $C_6H_6$  yields (1) (3)  $\gamma$ -chloroacetoacetanilide, cryst. from ether, m.p. 140-141° (1).

3:9088 (1) Hurd, Abernathy, *J. Am. Chem. Soc.* 62, 1147-1148 (1940). (2) Hurd, Williams, *J. Am. Chem. Soc.* 58, 962-968 (1936). (3) Boese, *Ind. Eng. Chem.* 32, 16-22 (1940).

3:9092 DIGLYCOLOYL DICHLORIDE  $C_4H_4O_2Cl_2$  Beil. S.N. 220

B.P. 116° at 12 mm. (1)

Colorless oily liq. with odor suggesting succinyl dichloride (3:6200).

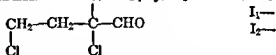
[For prepn. of  $\bar{C}$  from diglycolic acid (1:0495) by ausp. in  $\text{CHCl}_3$  and treatment with  $\text{PCl}_5$  see (1) (note also that insufficient  $\text{PCl}_5$  leads (1) to diglycolic anhydride, m.p.  $97^\circ$ , b.p.  $120^\circ$  at 12 mm. (3)); for mfg. from  $\alpha, \alpha'$ -dichlorodimethyl ether (3:5245) by treatment at  $25$ – $50^\circ$  and elevated press. with CO and suitable catalysts such as  $\text{AlCl}_3$  or  $\text{ZnCl}_2$  see (2).]

$\bar{C}$  with excess MeOH yields (1) (3) dimethyl diglycolate, m.p.  $35^\circ$  (3),  $36^\circ$  (1).

$\bar{C}$  with aq. readily hydrolyzes (1) yielding diglycolic acid (1:0495); for the anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see the acid (1:0495).

3:9092 (1) Anschütz, Biernaux, *Ann.* 273, 64–65 (1893). (2) Scott (to du Pont Co.), U.S. 2,084,284, June 15, 1937, *Cent.* 1937, II 2261; *C.A.* 31, 5383 (1937). (3) Darapsky, Stauber, *J. prakt. Chem.* (2) 146, 212 (1936).

3:9094  $\alpha, \alpha, \gamma$ -TRICHLORO-*n*-BUTYRALDEHYDE  $\text{Cl}$   $\text{C}_4\text{H}_5\text{OCl}_3$  Beil. I-665



No physical consts. on  $\bar{C}$  are reported; it is characterized only as a liquid which at  $-78^\circ$  becomes a glassy solid (1). — Spar. sol. aq. (1).

[For prepn. of  $\bar{C}$  from  $\alpha, \gamma$ -dichlorocrotonaldehyde [Beil. I-731], with dry HCl gas at  $0^\circ$  see (1).]

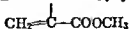
$\bar{C}$  oxidizes only very slowly in air but with fuming  $\text{HNO}_3$  in cold gives (1)  $\alpha, \alpha, \gamma$ -trichloro-*n*-butyric acid (3:1831), m.p.  $73$ – $75^\circ$  (1).

$\bar{C}$  does not add aq. to form a hydrate but on shaking with aatd. aq.  $\text{NaHSO}_3$  soln. evolves heat and ppts. a  $\text{NaHSO}_3$  cpd (1).

$\bar{C}$  on boilg. with aq. contg.  $\text{BaCO}_3$  gives an amorphous prod., very easily sol. in aq. and possessing carbohydrate characteristics; for details see (2).

3:9094 (1) Natterer, *Monatsh.* 4, 551 (1883). (2) Natterer, *Monatsh.* 5, 251–255 (1884).

3:9096 METHYL  $\alpha$ -CHLOROACRYLATE  $\text{Cl}$   $\text{C}_4\text{H}_5\text{O}_2\text{Cl}$  Beil. S.N. 163



B.P.  $57$ – $59^\circ$  at 55 mm. (1)

$D_4^{20} = 1.189$  (1)  $n_D^{20} = 1.4420$  (11)

$41$ – $44^\circ$  at 28 mm. (11)

1.4490 (1)

[For prepn. of  $\bar{C}$  from methyl  $\alpha, \beta$ -dichloropropionate (3:9103) by distn. with quinoline (yield: 73% (1), 60% (11)) or other dehydrochlorinating agent such as  $\text{Na}_2\text{CO}_3$  (2) see indic. refs.; from trichloroethylene (3:5170) with  $\text{CH}_2\text{O} + \text{MeOH} + \text{H}_2\text{SO}_4 + \text{CuCO}_3$  as directed (73% yield) see (10).]

$\bar{C}$  readily polymerizes on standing, especially in light or pres. of peroxides (for study of polymers and polymerization see (1)). For examples of industrial prepn. and use of polymers of  $\bar{C}$  for molding resins, etc., see (3) (4) (5) (6); for examples of co-polymers of  $\bar{C}$  with butadiene-1,3 or chloroprene (7), styrene (3), or vinyl acetate (9) see indic. refs.]

[For comments on other esters of  $\bar{C}$  see  $\alpha$ -chloroacrylic acid (3:1445).]

[For study of ester interchange of  $\bar{C}$  with various alcohols see (11).]

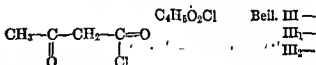
3:9096 (1) Marvel, Cowan, *J. Am. Chem. Soc.* 61, 3150–3160 (1939). (2) Pollack (to Pittsburgh Plate Glass Co.), U.S. 2,245,547, June 10, 1941; *C.A.* 35, 5908 (1941); *Brit.* 536,806, May 29, 1941; *C.A.* 36, 1614 (1942). (3) Röhm & Haas Co., *Brit.* 411,800, June 13, 1931; *Cent.* 1935,

I 1628-1629; C.A. 28, 6956 (1034). (4) Ireland, Brit. 527,494, Oct. 10, 1940; C.A. 35, 7065 (1941). (5) Stearn, *Pollock & Pittsburgh Plate Glass Co.* U.S. 2,202,800 (1940).

35,  
C.A.  
No.  
194  
264  
194  
No.  
194  
C.A. 38, 1751 (1944).  
(11) Frank, David, Drake, McPherson, *J. Am. Chem. Soc.* 66, 1509-1510 (1944).

## 3:9098 ACETOACETYL CHLORIDE

(β-Keto-n-butyryl chloride)



This compound cannot be preserved at temperatures above  $-20^\circ$  (1) cf. (4); m.p.  $-50$  to  $-51^\circ$  (1).

[For prepn. of  $\bar{\text{C}}$  from acetylketene (ketene dimer) (2) (3) (5) with dry HCl gas at  $-7$  to  $-50^\circ$  see (1).] [For anal. of  $\bar{\text{C}}$  by reactn. with dil. alk. see (1).]

$\bar{\text{C}}$  on warming to room temp. undergoes bimolecular condensation with elimination of 2 HCl and yields (1) dehydroacetic acid (1:0700), m.p.  $109^\circ$ .

$\bar{\text{C}}$  in dry ether at  $-60^\circ$  treated with abs. EtOH gives (27% yield (1)) ethyl acetoacetate (1:1710).

$\bar{\text{C}}$  in dry ether at  $-50^\circ$  treated with aniline gives (49% yield (1)) acetoacetanilide [Beil. VII 519 VII (1975) m.p.  $85^\circ$ ; note, however, that  $\bar{\text{C}}$  with aniline at room temp. yields

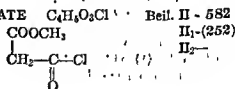
acid-3 (1-phenyllutidonecarboxylic acid-3) Eq. calcd. 243, found 235 (1).

$\bar{\text{C}}$  with  $\text{C}_6\text{H}_6 + \text{AlCl}_3$  or with  $\text{C}_6\text{H}_5\text{MgBr}$  in ether at  $-50^\circ$  gives (27% and 12% yield respectively (1)) benzoylacetone (1:1450), m.p.  $59^\circ$  (1).

3:9098 (1) Hurd, Kelso, *J. Am. Chem. Soc.* 62, 1548-1549 (1940). (2) Hurd, Abernathy, *J. Am. Chem. Soc.* 62, 1147-1148 (1940). (3) Hurd, Williams, *J. Am. Chem. Soc.* 58, 962-968 (1936). (4) Staudinger, Scholtz, *Ber.* 53, 1109 Note 1 (1920). (5) Boese, *Ind. Eng. Chem.* 32, 16-22 (1940).

## 3:9098-A METHYL (CHLOROFORMYL)ACETATE

(Carbomethoxyacetyl chloride)



B.P.  $57-59^\circ$  at 12 mm. (1)

[See also ethyl (chloroformyl)acetate (3:9246).]

Note that  $\bar{\text{C}}$  is both an acid chloride and an ester; it comprises the half acid chloride/half methyl ester of malonic acid (1:0480).

[For prepn. of  $\bar{\text{C}}$  from potassium salt of methyl hydrogen malonate with  $\text{SOCl}_2$  in dry ether (68% yield) see (1).]

$\bar{\text{C}}$  on htg. or on repeated distn. or by action of quinoline in dry ether at  $0^\circ$  loses HCl and undergoes condensation to methyl 6-methoxy-2,4-diketo-2,3-dihydropyran-3-carboxylate [Beil. XVIII<sub>1</sub>-(540)], ndls. from  $\text{CHCl}_3$ , m.p.  $143-150^\circ$  (1) cf. (2).

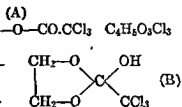
• ①  $\omega$ -(Carbomethoxyacet)anilide: ndls. from ether/pet. eth., m.p. 42-43° (1). [From  $\bar{C}$  with aniline (1).]

—  $\omega$ -(Carbomethoxyacet)-*p*-toluidide: unreported.

3:9098-A (1) Staudinger, Becker, *Ber.* 50, 1019-1020 (1917). (2) Leuchs, *Ber.* 39, 2643 (1906).

3:9099  $\beta$ -HYDROXYETHYL HOCH<sub>2</sub>CH<sub>2</sub>-O-CO.CCl<sub>3</sub> C<sub>4</sub>H<sub>5</sub>O<sub>3</sub>Cl<sub>3</sub> Beil. S.N. 160  
TRICHLOROACETATE 2691

(2-Hydroxy-2-(trichloromethyl)-1,3-dioxolane)



B.P. 130-140° at 12 mm. (1)  $n_D^{25} = 1.4762$  (3)  
89° at 1.75 mm. (2)  
83° at 0.8 mm. (2)  $D_4^{20} = 1.532$   $n_D^{20} = 1.48378$  (2)  
68° at 0.025 mm. (3) 1.4775 (3)

Note that  $\bar{C}$  may react either in the ester form (A) or the dioxolane form (B) and doubtless exists as a tautomeric equilibrium of both; in this equilibrium, however, form (A) probably predominates (2), but variations in the equilibrium may account for the observed variation in  $n_D^{20}$  (see above).

Colorless odorless oil, spar. sol. aq. (2). —  $\bar{C}$  on long stdg. is claimed (2) to disproportionate to ethylene glycol bis-(trichloroacetate) (not, however, otherwise described in the literature) and ethylene glycol (1:6465). —  $\bar{C}$  on attempted distn at usual water-pump vac. (14-17 mm.) (3) or  $\bar{C}$  in presence of a trace of pyridine (3) decomposes yielding monomeric ethylene glycol carbonate [Beil. XIX-100], m.p. 38°, and CHCl<sub>3</sub> (3:5050).

[For prepn. of  $\bar{C}$  from ethylene glycol (1:6465) with trichloroacetyl chloride (3:5420) in 1,4-dioxane soln. (82% yield (2)) or from ethylene oxide (1:6105) with trichloroacetic acid (3:1150) (28% yield based on latter (1) (3)) see indic. refs.]

$\bar{C}$  on shaking with aq. and simultaneously titrating with *N*/10 aq. NaOH hydrolyzes to ethylene glycol (1:6465) and trichloroacetic acid (3:1150) as shown by Sap. Eq. of 207.8 (2) (calcd. 207.5).

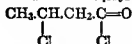
[ $\bar{C}$  with diazomethane (1) best in CCl<sub>4</sub> soln. (2) gives (yields: 78% (2), 39% (1)) the methyl ether corresp. to structure (B), viz., 2-methoxy-2-(trichloromethyl)-1,3-dioxolane, pr. tbs. from alc., m.p. 78-78.5° (1), 77-78° (2) (4), b.p. 114-115° at 12 mm. (4), 112-113° at 10 mm. (1); this product although resistant to saponification by alkalis is hydrolyzed by dil. acids (4). — Note that the isomeric methyl ether corresponding to structure (A), viz.,  $\beta$ -methoxyethyl trichloroacetate, although not obtainable from  $\bar{C}$ , has nevertheless been prepd. (82% yield (4)) from  $\beta$ -methoxyethanol (methyl "cellosolve") (1:6405) with trichloroacetyl chloride (3:5420), has quite different physical props., viz., m.p. 14-14.8° (4), b.p. 92-93° at 10 mm. (4), and is easily hydrolyzed (4) on sbaking with aq. alone to  $\beta$ -methoxyethanol (1:6405) and trichloroacetic acid (3:1150). — Note also that the first of the above two methyl ethers, i.e., 2-methoxy-2-(trichloromethyl)-1,3-dioxolane, by trans-esterification with alcohols (e.g., EtOH (2), *n*-PrOH (4), *n*-BuOH (2)) can be converted to its higher homologs.]

$\bar{C}$  with acid chlorides gives esters corresp. to the acyclic structure (A): e.g.,  $\bar{C}$  with AcCl (3:7065) gives (71% yield (4)) the mixed ester, ethylene glycol acetate-trichloroacetate ( $\beta$ -acetoxyethyl trichloroacetate) b.p. 122° at 11 mm. (4);  $\bar{C}$  with SOCl<sub>2</sub> gives (70% yield (4))  $\beta$ -chloroethyl trichloroacetate (3:6519).

3:9099 (1) Meerwein, Hinz, *Ann.* 484, 16-17 (1930). (2) Meerwein, Sönke, *J. prakt. Chem.* (2) 137, 295-298, 308-311 (1933). (3) Hibbert, *Grieg. Can. J. Research* 4, 261-263 (1931). (4) Meerwein, Sönke, *Ber.* 64, 2375-2381 (1931).

3:9100 *d,l*- $\beta$ -CHLORO-*n*-BUTYRYL CHLORIDE

Beil. II - 278

 $\Pi_1$ — $\Pi_2$ -(253)

B.P. 67–69° at 41 mm. (1)

 $D_4^{20.25} = 1.2163$  (4) $n_D^{20} = 1.4525$  (3)

65–67° at 40 mm. (2) (3)

1.4511 (4)

51–53° at 21 mm. (4) (6)

40–41° at 12 mm. (2)

[For prepn. of  $\bar{C}$  from  $\beta$ -chloro-*n*-butyric acid (3:0035) with  $\text{SOCl}_2$  (4) (6) (3) (90% yield (2)) see indic. refs.; from *n*-butyryl chloride (3:7370) with  $\text{SO}_2\text{Cl}_2$  + dibenzoyl peroxide in  $\text{CCl}_4$  (55% yield  $\bar{C}$  + 15%  $\alpha$ - (3:5570) and 30%  $\gamma$ - (3:5970) isomers (3)) or with  $\text{Cl}_2$  in  $\text{CCl}_4$  (1) see indic. refs.]

[ $\bar{C}$  with methyl *p*-tolyl ether (1:7495) +  $\text{AlCl}_3$  in  $\text{CS}_2$  yields (4) 3-( $\beta$ -chloro-*n*-butyryl)-4-methylphenol (b.p. 167–170° at 20 mm. (4)) which in alc. soln. on addn. of dil.  $\text{Na}_2\text{CO}_3$  loses  $\text{HCl}$  yielding 2,6-dimethylchromanone, m.p. 54–55° (5).]

$\bar{C}$  with benzene +  $\text{AlCl}_3$  in  $\text{CS}_2$  yields (6) (by Friedel-Crafts reactn. of both halogen atoms)  $\beta$ -phenylbutyrophenone (phenyl  $\beta$ -phenyl-*n*-propyl ketone) [Beil. VII-453], m.p. 74° (6).

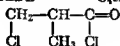
$\bar{C}$  on hydrolysis with aq. yields  $\beta$ -chloro-*n*-butyric acid (3:0035) q.v. (note, however, that hydrolysis with alk. will cause loss of  $\text{HCl}$  and formn. of crotonic acid (1:0425)).

For the anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see  $\beta$ -chloro-*n*-butyric acid (3:0035).

3:9100 (1) Michael, *Ber.* 34, 4052 (1901). (2) Abderhalden, Fleischmann, *Fermentforschung*, 10, 203 (1928); *Cent.* 1929, I 2318; *C.A.* 23, 1388 (1929). (3) Kharasch, Brown, *J. Am. Chem. Soc.* 62, 928 (1940). (4) von Auwers, *Ann.* 421, 37–39 (1921). (5) von Auwers, *Ber.* 52, 128 (1919). (6) von Auwers, Müller, *J. prakt. Chem.* (2) 137, 128 (1933).

3:9101  $\beta$ -CHLORO-ISOBUTYRYL CHLORIDE

Beil. II - 295

 $\Pi_1$ — $\Pi_2$ —

B.P. 171–172° at 765 mm. (1)

 $n_D^{20} = 1.4542$  (2)

151–152° (2)

Because of the serious disagreement in h.p. and the lack of data to decide between them,  $\bar{C}$  is placed in this division.

[For prepn. of  $\bar{C}$  from isobutyryl chloride (3:7270) with  $\text{Cl}_2$  in  $\text{CCl}_4$  soln. (30–40% yield  $\bar{C}$  + 60–70%  $\alpha$ -isomer (3:5385) (1)), with  $\text{Cl}_2$  in activating light (3) (6), or with  $\text{SO}_2\text{Cl}_2$  + dibenzoyl peroxide in  $\text{CCl}_4$  (80% yield  $\bar{C}$  + 20%  $\alpha$ -isomer (3:5385) (2)), see indic. refs.; for formn. of  $\bar{C}$  from phosgene (3:5000) + propylene + cat. see (5).]

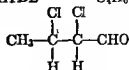
$\bar{C}$  as liq. with dehydrohalogenating cat. loses  $\text{HCl}$  giving (4)  $\alpha$ -methacryloyl chloride.

$\bar{C}$  with aniline gives (1) (2)  $\beta$ -chloro-isobutyranilide, m.p. 109.0–109.5° (2), 104–105° (1); note that the isomeric  $\alpha$ -dichloro-isobutyranilide has m.p. 71–71.5° (2), 69–70° (1).

3:9101 (1) Michael, Garner, *Ber.* 34, 4054–4055 (1901). (2) Kharasch, Brown, *J. Am. Chem. Soc.* 62, 925–929 (1940). (3) Schmidt, Schloffer (to I.G.), *Ger.* 738,398, July 15, 1943; *C.A.* 33, 3992 (1944). (4) I.G. French 873, 389, July 7, 1942; *Cent.* 1942, II 2535; not in *C.A.* (5) Reid (to du Pont Co.), U.S. 2,028,012, Jan. 14, 1936; *Cent.* 1936, II 866; *C.A.* 30, 1387 (1936). (6) Schmidt, Schloffer (to I.G.), *Ger.* 738,398, July 15, 1943; *C.A.* 38, 3992 (1944).

3:9102  $\alpha,\beta$ -DICHLORO-*n*-BUTYRALDEHYDE $C_4H_6OCl_2$ 

Beil. I —

(Crotonaldehyde dichloride;  
2,3-dichlorohutanal-1) $I_1 -$   
 $I_2 - (724)$ 

B.P. 58-60° at 20 mm. (1)

 $D_4^{21} = 1.2666$  (1) $n_D^{21} = 1.4618$  (1)

48-49° at 13 mm. (2)

 $D_4^{15} = 1.2716$  (1)

Colorless liq. with odor suggesting chloral. —  $\bar{C}$  on exposure to light or on distn. at ord. press. turns brown and decomposes with evoln. of HCl. —  $\bar{C}$  is insol. aq.; sol. alc., ether,  $\text{CHCl}_3$ , or  $\text{CCl}_4$ .

[For prepn. of  $\bar{C}$  from crotonaldehyde (1.9150) with  $\text{Cl}_2$  directly at  $-5^\circ$  (3) cf. (4), or in  $\text{CCl}_4$  soln. at  $0^\circ$  (98% yield (1)), or in  $\text{CS}_2$  in freezing mixt. (2) see indic. refs.]

$\bar{C}$  with  $\text{NaHSO}_3$  soln gives (2) a crystn. addn. compound.

[ $\bar{C}$  in MeOH contg. 1% HCl gas refluxed 4 hours gives (40% yield (5))  $\alpha,\beta$ -dichloro-*n*-butyraldehyde dimethylacetal, oil, b.p. 86-90° at 13 mm.,  $D_4^{19.5} = 1.179$ ,  $n_D^{19.5} = 1.4498$  (5); note that the presumably corresp. behavior of  $\bar{C}$  with EtOH and the  $\alpha,\beta$ -dichloro-*n*-butyraldehyde diethylacetal are unreported]

[ $\bar{C}$  with ethylene glycol (1:6465) at 100° for 1 hour even in absence of cat. gives (50.3% yield (3)) corresp. cyclic acetal, viz., 2-( $\alpha,\beta$ -dichloro-*n*-propyl)-1,3-dioxolane, b.p. 100-105° at 13-15 mm. (3).]

[ $\bar{C}$  with aq. NaOAc on distn. with steam splits out 1 HCl giving (70-80% yield (6)) (1) (3) (7)  $\alpha$ -chlorocrotonaldehyde (3.8117), b.p. 147-150° at 760 mm. (3).]

[ $\bar{C}$  with  $\text{EtMgBr}$  in dry ether followed by usual hydrolysis gives (80% yield (2)) 4,5-dichlorohexanol-3 [Beil. I-439], b.p. 88-93° at 12 mm.,  $D_4^{19} = 1.1685$ ,  $n_D^{19} = 1.4709$  (2). — Similarly,  $\bar{C}$  with  $\text{C}_6\text{H}_5\text{MgBr}$  gives (66% yield (2))  $\alpha,\beta$ -dichloro-*n*-propyl-*p*-benzyl-carbinol, b.p. 162-168° at 14 mm.,  $D_4^{15} = 1.2355$ ,  $n_D^{15} = 1.5500$  (2)]

[Note that suitable oxidn. of  $\bar{C}$  would be expected to yield either or both crotonic acid dichloride (3:1375), m.p. 63°, or isocrotonic acid dichloride (3:1903), m.p. 78°, but that such oxidation has not actually been reported.]

[For use of  $\bar{C}$  as component of insecticides see (8).]

—  $\alpha,\beta$ -Dichloro-*n*-butyraldoxime: oil, not further characterized (2).

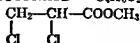
—  $\alpha,\beta$ -Dichloro-*n*-butyraldehyde phenylhydrazone: unreported [Note, however, that  $\bar{C}$  reacts vigorously with phenylhydrazine (2).]

①  $\alpha,\beta$ -Dichloro-*n*-butyraldehyde semicarbazone: m.p. 96-97° (2).

3:9102 (1) Moureu, Murat, Tampier, *Bull. soc. chim.* (4) 29, 31-32 (1921). (2) Helferich, *Ber.* 57, 1277-1278 (1924). (3) Hubbert, Houghton, Taylor, *J. Am. Chem. Soc.* 51, 613 (1929). (4) Ziesel, *Monatsh.* 7, 360 (1886). (5) Naftali, *Bull. soc. chim.* (5) 4, 338 (1937). (6) Chattaway, Irving, Outhwaite, *J. Chem. Soc.* 1933, 994. (7) Chem. Fabrik vorm. Weilerter-Meer, Ger. 351, 137, April 3, 1922; *Cent.* 1922, IV 155, not in C.A. (8) Soc. des Usines Chim. Rhône-Poulenc, Ger. 528, 194, June 26, 1931; *Cent.* 1931, II 1910, [C.A. 25, 4653 (1931)].

3:9103 METHYL *d,l*- $\alpha,\beta$ -DICHLOROPROPIONATE $C_4H_6O_2Cl_2$ 

Beil. S.N. 162



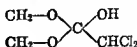
B.P. 72-75° at 21 mm. (1)

[For prepn. of  $\bar{C}$  from technical methyl acrylate (1:3025) in MeOH soln. below 40° by treatment with  $\text{Cl}_2$  (85% yield) see (1).]





:9107  $\beta$ -HYDROXYETHYL DICHLOROACETATE  $C_4H_5O_3Cl_2$  (A) Beil. S.N. 160  
(2-Hydroxy-2-(dichloromethyl)-1,3-dioxolane) (B) Beil. S.N. 2691



(A)

(B)

B.P. 106° at 0.08 mm. (1) (3)  
82° at 0.5 mm. (2)  
81-82° at 0.5 mm. (2)

$D_4^{20} = 1.438$  (2)  
1.429 (2)

$n_D^{25} = 1.4730$  (1)  
 $n_D^{23} = 1.4743$  (3)  
 $n_D^{20} = 1.47345$  (2)  
1.47253 (2)

Note that  $\bar{C}$  may react either in the acyclic ester form (A) or the dioxolane form (B) and doubtless exists as a tautomeric equilibrium of both; in such an equilibrium, however, form (A) greatly predominates (2); but variations may account for the variation in constants (see above).

Colorless oil, spar. sol. aq. —  $\bar{C}$  on long stdg. is claimed (2) to disproportionate to ethylene glycol bis-(dichloroacetate) (not, however, further described in the literature) and ethylene glycol (1:6465).

[For prepn. of  $\bar{C}$  from ethylene glycol (1:6465) with dichloroacetyl chloride (3:5290) in 1,4-dioxane soln. (75% yield (2)) or from ethylene oxide (1:6105) with dichloroacetic acid (3:6208) (yields: 34% (2), 15% (1)) see indic. refs.]

$\bar{C}$  on shaking with aq. and simultaneously titrating with  $N/10$  aq. NaOH hydrolyzes to ethylene glycol (1:6465) and dichloroacetic acid (3:6208) as shown by Sap. Eq. of 170.8 (2) (calcd. 173).

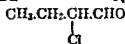
[ $\bar{C}$  with diazomethane gives not only the methyl ethers of both forms (A) and (B) but also other unexpected products including ethylene glycol (1:6465), ethylene glycol dimethyl ether (1:6141), methyl dichloroacetate (3:5655), etc. Note that the methyl ether of structure (B), viz., 2-methoxy-2-(dichloromethyl)-1,3-dioxolane, has b.p. 91-92.5° at 9 mm. (2),  $D_4^{20} = 1.387$  (2),  $n_D^{20} = 1.47032$ , and is stable to aq. alk.; that corresp. to the acyclic structure (A), viz.,  $\beta$ -methoxyethyl dichloroacetate (methyl-"cellosolve" dichloroacetate), best prepared (100% yield (2)) from  $\beta$ -methoxyethanol (1:6405) with dichloroacetyl chloride (3:5290) in  $CHCl_3$ , has h.p. 55-56° at 0.5 mm. (2),  $D_4^{20} = 1.309$  (2),  $n_D^{20} = 1.45157$  (2).]

3:9107 (1) Allen, Hibbert, *J. Am. Chem. Soc.* 56, 1399 (1934). (2) Meerwein, Sonke, *J. prakt. Chem.* (2) 137, 298-301, 311-316 (1933). (3) Hibbert, Greig, *Can. J. Research* 4, 262 (1931).

3:9109  $\alpha$ -CHLORO-*n*-BUTYRALDEHYDE  
(2-Chlorobutanal-1)



Beil. S.N. 87



No record of this compound can be found in the literature. However, for the isomeric  $\beta$ -chloro-*n*-butyraldehyde (3:9110),  $\gamma$ -chloro-*n*-butyraldehyde (3:9111), and  $\alpha$ -chloro-isobutyraldehyde (3:7235) see indic. refs.

3:9110  $\beta$ -CHLORO-*n*-BUTYRALDEHYDE

(3-Chlorobutanal-1)



Beil. I —

I<sub>1</sub>—I<sub>2</sub>-(724)

B.P. 28-33° at 13 mm. (1)

[See also the trimer of  $\bar{C}$  (3:2650).]

Spar. sol. aq. but misc. with org. solvents.

[For prepn. of  $\bar{C}$  from crotonaldehyde (1:0150) with 1 mole HCl in ether (50% yield) see (1).] $\bar{C}$  is difficult to preserve because of rapid polymerization to its trimer, para- $\beta$ -chloro-*n*-butyraldehyde (3:2650), m.p. 96-97°. [The product supposed by (2) to have been  $\bar{C}$  was actually (1) this trimer.][ $\bar{C}$  with 3 moles acetaldehyde (1:0100) in the cold gives (53% yield (1)) 2,4-dimethyl-6-( $\beta$ -chloro-*n*-propyl)trioxane-1,3,5 [Beil. S.N. 2952], b.p. 83-85° at 13 mm.,  $D_4^{19} = 1.0937$ ,  $n_D^{19} = 1.4373$  (1).][ $\bar{C}$  with excess EtMgBr yields (1) 5-chlorohexanol-3 [Beil. I<sub>2</sub>-(438)] h.p. 78-79° at 13 mm.,  $D_4^{19} = 1.0012$ ,  $n_D^{19} = 1.4433$  (1), together with other products.] $\bar{C}$  with methylhydrazine in dry ether yields (3) 1,5-dimethylpyrazoline, b.p. 124-132° (picrate, m.p. 112-113° (3)).3:9110 (1) Helferich, Besler, *Ber.* 57, 1280 (1924). (2) Kekulé, *Ann.* 162, 100-102 (1872). (3) von Auwers, Helmke, *Ann.* 453, 204 (1927).3:9111  $\gamma$ -CHLORO-*n*-BUTYRALDEHYDE

(4-Chlorobutanal-1)



Beil. S.N. 87



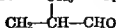
B.P. 50-51° at 13 mm. (1)

 $D_{15}^{85} = 1.107$  (1) $n_D^{85} = 1.44662$  (1)[For prepn. of  $\bar{C}$  from 5-chloropentanediol-1,5 (1) by oxidn with  $Ph(OAc)_4$  see (1).]  
 $\bar{C}$  polymerizes readily on htg. (1).①  $\gamma$ -Chloro-*n*-butyraldoxime: m.p. 74.5° (1).②  $\gamma$ -Chloro-*n*-butyraldehyde *p*-nitrophenylhydrazone: m.p. 110° (1).③  $\gamma$ -Chloro-*n*-butyraldehyde 2,4-dinitrophenylhydrazone: m.p. 134-135° (1).3:9111 (1) Paul, *Compt. rend.* 215, 303-305 (1942); *C.A.* 38, 4907 (1944).3:9112  $\beta$ -CHLORO-ISOBUTYRALDEHYDE

(3-Chloro-2-methylpropanal-1)



Beil. S.N. 87

No physical constants for  $\bar{C}$  are recorded.[For prepn. of  $\bar{C}$  from 3-chloro-2-methylpropen-2-ol-1 (3:8340) by treatment with acids as specified see (1).]No other record of  $\bar{C}$  appears in the literature.3:9112 (1) N. V. de Bataafsche Petroleum Maatschappij, French 763,286, April 26, 1934; *Cent.* 1934 II 1531; [*C.A.* 28, 5077 (1934)].

3:0860	CHLORAL ETHYLALCOHOLATE	$C_4H_7O_2Cl_3$	Beil. I - 621
	(Chloral alcoholate; tri-chloroacetaldehyde (mono)ethylacetal)	$Cl_3C.CH(OH)-OC_2H_5$	$I_1-(330)$ $I_2-(681)$

M.P. 56-57°	(1)	B.P. 115-117°	(1)
50°	(2) (3)	116.8°	at 771 mm. (5)
47.5°	(4)	116-116°	(9)
46.6°	(5)	111.0	at 741.4 mm. (4)
46°	(6) (7)		
45.2°	(10)		
46°-46.5°	(8)		
40°	(9)		

[See also chloral (3:5210) and chloral hydrate (3:1270).]

### PREPARATION

From chloral. [For prepn. of  $\bar{C}$  from chloral (3:5210) with EtOH (1:6130) (yields: 100% (11), 71.3% with 95% EtOH refluxed 2 hrs (4) (9) (12)) see indic. refs.; for influence of solvents see (13) (14); for formn. of  $\bar{C}$  from chloral (3:5210) + AcH + Al(OEt)<sub>3</sub> see (8).]

From chloral hydrate. [For prepn. of  $\bar{C}$  from chloral hydrate (3:1270) with EtOH (1:6130) (yield: 75% in 60 min., 38% in 24 hrs. reflux (4)), with triethyl orthoformate (1:3241) (25% yield in 105 min. reflux (4)), or with tetraethyl orthosilicate (4% yield in 4 hrs. reflux (4)) see indic. refs.]

From ethyl alcohol. [For formn. of  $\bar{C}$  as end prod. of reaction of ethyl alcohol (1:6130) with Cl<sub>2</sub> see (15).]

### PHYSICAL PROPERTIES

$\bar{C}$  is less sol. in aq. than chloral hydrate (3:1270) (6) (7). — [For study of toxicity of  $\bar{C}$  as compared with chloral hydrate (3:1270) see (29).]

### CHEMICAL BEHAVIOR

Dissociation.  $\bar{C}$  on distillation (7) or in some solns. in org. solvents cf. (17) (2) (18) is partially dissociated into chloral (3:5210) and EtOH (1:6130).

#### BEHAVIOR WITH INORGANIC REACTANTS

With H<sub>2</sub>SO<sub>4</sub>.  $\bar{C}$  with cold conc. H<sub>2</sub>SO<sub>4</sub> yields (1) chloral (3:5210) (or its polymerization products) and EtHSO<sub>4</sub>.

With aq. alkali.  $\bar{C}$  with aq. alkali gives (6) CHCl<sub>3</sub> (3:5050) + salts of formic acid (1:1005).

With chlorine. [ $\bar{C}$  with Cl<sub>2</sub> at 80° gives (19) trichloroacetaldehyde diethylacetal (3:6317).]

With PCl<sub>5</sub>. [ $\bar{C}$  with PCl<sub>5</sub> in ether below 20° (20) (4) cf. (21) (22) gives (yields: 55-74% (20), 25-33% (11))  $\alpha,\beta,\beta,\beta$ -tetrachloroethyl ethyl ether [Beil. I-623, I<sub>2</sub>-(681)], b.p. 189.7° at 758.7 mm. (21), 189.4° at 749.1 mm. cor. (20), 184° at 738 mm. (4), 79° at 16 mm. (20);  $D_4^{25} = 1.4225$  (20).]

#### BEHAVIOR WITH ORGANIC REACTANTS

With other alcohols. [ $\bar{C}$  with other alcohols may undergo an exchange of alkyl radicals; for studies of such interchange see (4) (21).]

[For prepn. of  $\bar{C}$  from either the low-boilg. (3:5360) or high-boilg. (3:5615) stereoisomers of 1,2-dichlorobutene-2 (together with 2-chlorobutene-2-ol-1 (3:8240)) by hydrolysis with 2 pts. aq. + 1 mole  $\text{CaCO}_3$  for 4 hrs. at  $70^\circ$  see (1); note that  $\bar{C}$  is formed by virtue of allylic transposition during the process and that *Cent.* and *C.A.* do not agree on the boilg. pt. (orig. inaccessible).

① 3-Chlorobuten-3-yl-2 *N*-( $\alpha$ -naphthyl)carbamate: m.p.  $92-92.5^\circ$  (1).

3:9115 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 7, 658-662 (1937); *Cent.* 1937, II 371; *C.A.* 31, 5754 (1937).

### 3:9130 *d,l*- $\alpha$ -CHLORO-*n*-BUTYRIC ACID



Beil. II - 276



$\text{H}_1$ -(123)

$\text{H}_2$ -(253)

B.P.  $109.5^\circ$  at 24 mm. (1)

$D_4^{20} = 1.1796$  (13)

$n_D^{20} = 1.4411$  (13)

$101.25^\circ$  at 15 mm. (2)

Viscous liq.; spar. sol. cold aq.; eas. sol. hot aq.

[For prepn. of  $\bar{C}$  from diethyl  $\alpha$ -ethyl- $\alpha$ -chloromalonate by hydrolysis and subsequent btg. of the resultant  $\alpha$ -ethyl- $\alpha$ -chloromalononic acid (90% yield (1)) (2) see indio. refs.; from *n*-butyric acid (1:1035) with  $\text{SO}_2\text{Cl}_2$  + acetyl chloride (3:7065) (3) or with  $\text{SO}_2\text{Cl}_2$  + dibenzoyl peroxide in  $\text{CCl}_4$  (10%  $\bar{C}$  + 45%  $\beta$ - (3:0035) and 45%  $\gamma$ - (3:0020) isomers) see (4); from *n*-butyric acid with  $\text{Cl}_2$  and suitable cat. see (5); from  $\alpha$ -chloro-*n*-butyryl chloride (3:5570) by hydrolysis with aq. see (7).]

$\bar{C}$  with  $\text{SOCl}_2$  (1) yields  $\alpha$ -chloro-*n*-butyryl chloride (3:5570), b.p.  $129-132^\circ$ .

[ $\bar{C}$  (in the form of  $\text{Ca}\bar{A}_2$ ) on cat. hydrogenation with  $\text{Pd}/\text{BaSO}_4$  in aq. alc. is completely converted (6) to *n*-butyric acid;  $\bar{C}$  itself is only partially (6) reduced.]

[For study of rate of hydrolysis of the halogen in  $\text{Na}\bar{A}$  by aq. at  $70^\circ$  see (8).]

— Methyl *d,l*- $\alpha$ -chloro-*n*-butyrate: b.p.  $145-146^\circ$  at 756 mm. (See 3:8103.)

— Ethyl *d,l*- $\alpha$ -chloro-*n*-butyrate: b.p.  $163-164^\circ$  at 760 mm. (See 3:8307.) For study of rate of esterification of  $\bar{C}$  with  $\text{EtOH}$  see (9).]

① *d,l*- $\alpha$ -Chloro-*n*-butyramide: cryst. from  $\text{C}_6\text{H}_6$ , m.p.  $81^\circ$  (10),  $78.4-78.9^\circ$  (11). [From methyl  $\alpha$ -chloro-*n*-butyrate (3:8103) with conc. aq.  $\text{NH}_4\text{OH}$  (60% yield (10)).]

② *d,l*- $\alpha$ -Chloro-*n*-butyranilide: m.p. not reported. [From  $\alpha$ -chloro-*n*-butyryl chloride (3:5570) with aniline (1).]

③ *d,l*- $\alpha$ -Chloro-*n*-butyro-*p*-toluidide: m.p.  $98^\circ$  (12).

3:9130 (1) Blaise, *Bull. soc. chim.* (4) 15, 668 (1914). (2) Cloves, *Ann.* 319, 357-358 (1901).

(3) Blank, *Ger.* 157,816, Jan. 18, 1905; *Cent.* 1905, I 414. (4) Kharasch, Brown, *J. Am. Chem. Soc.* 62, 925-929 (1940). (5) Bass (to Dow Chem. Co.), U.S. 2,010,685, Aug. 6, 1935; *Cent.* 1936, I 880; *C.A.* 29, 6608 (1935). (6) Paul, Schiedewitz, *Ber.* 62, 1937-1938 (1929). (7)

Markownikow, *Ann.* 153, 241 (1870). (8) Simpson, *J. Am. Chem. Soc.* 40, 679 (1918). (9) Lichty, *Ann.* 319, 372 (1901). (10) De Boosere, *Bull. soc. chim. Belg.* 32, 44-45 (1923).

(11) Vandewijer, *Bull. soc. chim. Belg.* 45, 255 (1936). (12) Wolfenstein, *Rolle, Ber.* 41, 736 (1908). (13) Schlanberg, *Z. physik. Chem.* A-172, 231 (1935).

### — *d,l*- $\beta$ -CHLORO-*n*-BUTYRIC ACID



Beil. II - 277



$\text{H}_1$ -(123)

$\text{H}_2$ -(253)

B.P.  $116^\circ$  at 22 mm.

M.P.  $16-16.5^\circ$

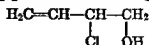
$D_4^{20} = 1.1898$

$n_D^{20} = 1.4421$

See 3:0035. Division A: Solids.

3:9113 *d,l*-2-CHLOROBUTEN-3-OL-1 $C_4H_7OCl$ 

Beil. S.N. 25



B.P. 69.5–70.0° at 30 mm. (1) (2)

60.5–67.0° at 30 mm. (3)

 $n_D^{20} = 1.4665$  (1) (2)

[See also 1-chlorobuten-3-ol-2 (3:8110).]

[For prepn. of  $\bar{C}$  from 3,4-epoxybutene-1 (1) (2) with conc. HCl (2 moles) in ether below 5° (61% yield (2)) or with cold conc. HCl (60% yield (3)) see indic. refs.; note that by these methods  $\bar{C}$  is accompanied by a small amt. (2% (2)) of 4-chlorobuten-2-ol-1 (1-chlorobuten-2-ol-4) (3:9114).]

$\bar{C}$  with  $Br_2$  gives (3) 2-chloro-3,4-dibromobutanol-1, b.p. 133.5–135.5° at 10 mm. (3).

$\bar{C}$  with KOH (3) loses HCl, ring-closing to 3,4-epoxybutene-1, b.p. 67° at 750 mm. (3), 65.0–65.8° at 739 mm. (2);  $D_4^{20} = 0.8745$  (2) (3);  $n_D^{20} = 1.4170$  (2) cf. (3).

[For study of hydrolysis of  $\bar{C}$  with aq. NaOH see (1).]

— 2-Methoxybuten-3-ol-1 ( $\bar{C}$  methyl ether): h.p. 70° at 50 mm. (2);  $n_D^{20} = 1.4290$  (2): corresp. 3,5-dinitrobenzoate, m.p. 68–71° (2). [From  $\bar{C}$  with MeOH/NaOMe refluxed 30 min. (52% yield (2))]

— 1-Chlorobuten-3-yl-1 acetate: h.p. 79.5–80° at 30 mm. (3). [Note that with KOH this prod. loses AcOH, ring-closing (3) to 3,4-epoxybutene-1 (above).]

— 1-Chlorobuten-3-yl-1 3,5-dinitrobenzoate: m.p. 65.6° u.c. (2). [Note that this prod. depresses m.p. of corresp. deriv. (m.p. 61.5–63.5° u.c.) from 1-chlorobuten-3-ol-2 (3:8110).]

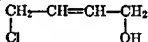
3:9113 (1) Kadesch, *J. Am. Chem. Soc.* 68, 46–48 (1946) (2) Kadesch, *J. Am. Chem. Soc.* 68, 41–45 (1946). (3) Petrov, *J. Gen. Chem. (U.S.S.R.)* 11, 991–995 (1941); *C.A.* 37, 1699 (1943).

## 3:0114 4-CHLOROBUTEN-2-OL-1

 $C_4H_7OCl$ 

Beil. S.N. 25

(1-Chlorobuten-2-ol-4)



B.P. 07–69° at 4–6 mm. (2)

64–65° at 2 mm. (2)

54–55° at 2 mm. (1)

 $n_D^{20.5} = 1.4792$  (1) $n_D^{20} = 1.4845$  (2)

[For form. of  $\bar{C}$  in small amount (18.6% yield (2)) from 3,4-epoxybutene-1 with HCl see (1) (2); note that the main product of this reaction is 2-chlorobuten-3-ol-1 (3:9113) (1) (2).]

[For study of hydrolysis of  $\bar{C}$  with aq. or aq. NaOH see (2).]

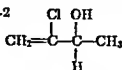
— 4-Chlorobuten-2-yl-1 3,5-dinitrobenzoate: unreported.

Ⓢ 4-Chlorobuten-2-yl-1 *N*-( $\alpha$ -naphthyl)carbamate: m.p. 88–89° (1).

3:9114 (1) Kadesch, *J. Am. Chem. Soc.* 68, 45 (1946). (2) Kadesch, *J. Am. Chem. Soc.* 68, 46–48 (1946)

3:9115 *d,l*-3-CHLOROBUTEN-3-OL-2 $C_4H_7OCl$ 

Beil. S.N. 25



B.P. 53–57° at 19 mm. (1)

67–68° at 19 mm. (1)

 $D_4^{23} = 1.1138$  (1) $n_D^{23} = 1.46232$  (1)

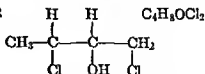
Colorless liq. insol. aq.

[For prepn. (93% yield (1)) from  $\beta$ -methoxyethanol (methyl "cellosolve") (1:6405) + phosgene (3:5000) see (1).]

①  $\beta$ -Methoxyethyl carhamate: from  $\bar{C}$  + aq.  $NH_4OH$  in poor yield (13.3% (1)); m.p. 46.8° (1).

3:9140 (1) Ashburn, Collett, Lazzell, *J. Am. Chem. Soc.* **60**, 2933-2934 (1938).

3:9145 1,3-DICHLOROBUTANOL-2



Beil. I-373

I<sub>1</sub>—  
I<sub>2</sub>—

B.P. 63-64° at 10 mm. (1)

$D_4^{15} = 1.2870$  (1)

$n_D^{20} = 1.4766$  (1)

$n_D^{15} = 1.4790$  (1)

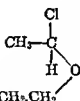
[For prepn. of  $\bar{C}$  from 3-chloro-1,2-epoxybutane ( $\alpha$ -chloroethylethylene oxide) or from 1-chloro-2,3-epoxybutane ( $\alpha$ -(chloromethyl)- $\alpha'$ -methyleneethylene oxide) by addn. of HCl see (1); for possibly similar processes cf. (2).]

$\bar{C}$  on oxidn. gives (1) 1,3-dichlorobutanone-2 (3:5900).

— 1,3-Dichloro-sec.-butyl acetate: b.p. 82.5-83.5° at 10 mm.,  $D_4^{20} = 1.2185$ ,  $D_4^{15} = 1.2229$ ;  $n_D^{20} = 1.4530$ ,  $n_D^{15} = 1.4550$  (1).

3:9145 (1) Petrov, *J. Am. Chem. (U.S.S.R.)* **11**, 713-721 (1941); *Cent.* **1942**, I 2867; *C.A.* **36**, 404 (1942). (2) Zikes, *Monatsh.* **6**, 348-355 (1885).

3:9150  $\alpha,\beta'$ -DICHLORODIETHYL ETHER  
( $\alpha$ -Chloroethyl- $\beta$ -chloroethyl ether)



Beil. I —

I<sub>1</sub>—

I<sub>2</sub>-(674)

B.P. 55-57° at 17 mm. (1)

$D_4^{20} = 1.1867$  (2)

$n_D^{20} = 1.4473$  (2)

51° at 10 mm. (2)

$D_{19}^{19} = 1.1823$  (1)

$n_D^{16.2} = 1.4497$  (1)

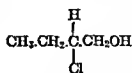
Colorless liq. fume. in air and decomposing on distn. at ord. press. (1).

[For prepn. (60% yield (2)) from ethylene chlorohydrin (3:5552) + acetaldehyde (1:0100) (2) or paraldehyde (1:0170) (1) + dry HCl see (1) (2).]

$\bar{C}$  rapidly dis. in cold aq. yielding by hydrolysis  $\beta$ -chloroethanol (3:5552), acetaldehyde (1:0100), and HCl (1).

3:9150 (1) Grignard, Purdy, *Bull. soc. chim.* (4) **31**, 984-985 (1922). (2) Lingo, Henze, *J. Am. Chem. Soc.* **61**, 1574-1575 (1939).

3:9100 2-CHLOROBUTANOL-1  
( $\beta$ -Chloro-*n*-butyl alcohol)



Beil. S.N. 24

B.P. 74-76° at 25 mm. (1)

$D_4^{25} = 1.062$  (1)  $n_D^{25} = 1.4410$  (1)

[For prepn. of  $\bar{C}$  (83% yield (1)) by saponification of the corresp. trichloroacetate obtd. by chlorination of *n*-butyl trichloroacetate (3:6315) see (1).]

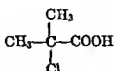
—  $\gamma$ -CHLORO-*n*-BUTYRIC ACID $\text{C}_4\text{H}_7\text{O}_2\text{Cl}$ 
 Beil. II - 278  
 II<sub>1</sub>-(124)  
 II<sub>2</sub>-(253)

B.P. 196° at 22 mm.

M.P. 16°

 $D_4^{20} = 1.2236$  $n_D^{20} = 1.4512$ 

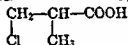
See 3:0020. Division A: Solids.

—  $\alpha$ -CHLORO-ISOBUTYRIC ACID $\text{C}_4\text{H}_7\text{O}_2\text{Cl}$ 
 Beil. II - 294  
 II<sub>1</sub>—  
 II<sub>2</sub>—

B.P. 118° at 50 mm.

M.P. 31°

See 3:0235. Division A: Solids.

3:9132  $\beta$ -CHLORO-ISOBUTYRIC ACID $\text{C}_4\text{H}_7\text{O}_2\text{Cl}$ 

Beil. S.N. 162

B.P. 128-133° at 50 mm. (1)

[For prepn. of  $\tilde{\text{C}}$  from isobutyric acid (1:1030) with  $\text{Cl}_2$  in pres. of S (2) (3) or in activating light (1) (note that some  $\alpha$ -chloro-isobutyric acid (3:0235) is also formed) see indie. refs.; for prepn. of  $\tilde{\text{C}}$  from isobutyric acid (1:1030) with  $\text{SO}_2\text{Cl}_2$  in presence of dibenzoyl peroxide in  $\text{CCl}_4$  soln. (85% yield  $\tilde{\text{C}}$  + 15%  $\alpha$ -isomer) see (4)]

$\tilde{\text{C}}$  should by conventional means such as  $\text{SOCl}_2$ , etc., be convertible to the corresp.  $\beta$ -chloroisobutyryl chloride (3:9101), but no record of such transformation appears in the literature, the expected product having been prepd. by indirect means.

— Methyl  $\beta$ -chloroisobutyrate: b.p. 151-155° at 750 mm., 85-90° at 60 mm.,  $D_{15}^{15} = 1.1101$   $n_D^{15} = 1.4297$  (1). [From  $\tilde{\text{C}}$  in MeOH with  $\text{H}_2\text{SO}_4$  in 70% yield (1) cf. (3); note that this prod. on btg. with quinoline (1) or passing over bot silica gel (3) loses HCl giving (87% yield (1)) methyl methacrylate.]

— Ethyl  $\beta$ -chloroisobutyrate: b.p. 56-58° at 10 mm. (5). [From ethyl  $\beta$ -hydroxyisobutyrate with  $\text{PCl}_5$  in dry ether (40% yield (5)).]

—  $\beta$ -Chloroisobutyramide: unreported.

—  $\beta$ -Chloroisobutyranilide: m.p. 109.0-109.5° (4), 104-105° (6).

—  $\beta$ -Chloroisobutyr-*p*-toluidide: unreported.

..

-1044 (1937). *Cent.* 1938, II  
 "acid has been erroneously  
 isoooleic acid" throughout.

(2) Loder, Ries (to du Pont Co), U.S. 2,043,670, June 9, 1936, *Cent.* 1936, II 2229, C.A. 30, 5240 (1936). (3) Loder (to du Pont Co), Brit. 428,223, June 6, 1935; *Cent.* 1936, I 179; C.A. 29, 6607 (1935). (4) Kharasch, Brown, *J. Am. Chem. Soc.* 62, 925-929 (1940). (5) Rydon, *J. Chem. Soc.* 1936, 1448. (6) Michael, Garner, *Ber.* 34, 4054-4055 (1901).

3:9140  $\beta$ -METHOXYETHYL CHLOROFORMATE $\text{C}_4\text{H}_7\text{O}_3\text{Cl}$ 

Beil. S.N. 199

(Methyl "cellosolve" chloroformate;

 $\text{CH}_3\text{O.CH}_2\text{CH}_2\text{O.CO.Cl}$  $\beta$ -methoxyethyl chlorocarbonate)



(3) (4) (8)) see (3) (4) (8); from tetramethylene glycol (1:6516) with  $\text{SOCl}_2$  + pyridine (47% yield (1)) or  $\text{S}_2\text{Cl}_2$  (2) see (1) (2); from  $\delta$ -chlorobutyl acetate by alcoholysis with  $\text{MeOH}$  (80% yield) see (6); for mfg. from ethylene oxide +  $\text{C}_2\text{H}_5\text{Cl}$  +  $\text{AlCl}_3$  (or other catalysts) see (9).]

$\bar{\text{C}}$  (2 moles) treated with  $\text{PBr}_3$  (1 mole) gives (98% yield (3)) tetramethylene chlorobromide, b.p. 175–176°,  $D_4^{20} = 1.488$ ,  $n_D^{20} = 1.4885$  (3). [For study of reaction of  $\bar{\text{C}}$  with  $\text{HBr}$  see (7).]

—  $\delta$ -Chloro-*n*-butyl acetate: oil, b.p. 92–93° at 22 mm. (6), 92–94° at 22 mm. (10);  $D_4^{20} = 1.0805$  (6);  $n_D^{20} = 1.43439$  (6). [From tetrahydrofuran [Beil. XVII-10] with  $\text{AcCl}$  (6) as directed cf. (10) or with  $\text{AcOH}$  +  $\text{HCl}$  + cat. (11).]

—  $\delta$ -Chloro-*n*-butyl benzoate: oil, b.p. 140–142.5° at 4 mm.,  $D_4^{20} = 1.1429$ ,  $n_D^{20} = 1.52028$  (6). [From tetrahydrofuran [Beil. XVII-10] with benzoyl chloride +  $\text{ZnCl}_2$  (54.5% yield (6)).]

—  $\delta$ -Chloro-*n*-butyl *p*-nitrobenzoate: oil, b.p. 205–206° at 7 mm. (12). [From tetrahydrofuran [Beil. XVII-10] with *p*-nitrobenzoyl chloride +  $\text{SnCl}_2$  (12).]

—  $\delta$ -Chloro-*n*-butyl 3,5-dinitrobenzoate: unreported.

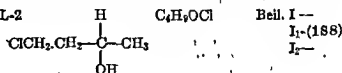
①  $\delta$ -Chlorobutyl *N*-phenylcarbamate: cryst. from pet. eth. (1); m.p. 54° (1), 54–55° (5).

②  $\delta$ -Chlorobutyl *N*-( $\alpha$ -naphthyl)carbamate: cryst. from pet. eth. (1); m.p. 69–70° (1), 69° (3); 66° (2).

3:9170 (1) Kirner, Richter, *J. Am. Chem. Soc.* 51, 2505–2506 (1929). (2) Bennett, Heathcoat, *J. Chem. Soc.* 1929, 272. (3) Starr, Hixon, *J. Am. Chem. Soc.* 56, 1595–1596 (1934). (4) Starr, Hixon, *Org. Syntheses*, Coll. Vol. 2 (1st ed.), 571–572 (1943). (5) Waddle, Adkins, *J. Am. Chem. Soc.* 61, 3363 (1939). (6) Cloke, Pilgrim, *J. Am. Chem. Soc.* 61, 2667–2669 (1939). (7) Bennett, Reynolds, *J. Chem. Soc.* 1935, 139. (8) Yur'ev, Minacher, Samurskaya, *J. Gen. Chem. (U.S.S.R.)* 9, 1710–1716 (1939); *C.A.* 34, 3731 (1940). (9) I.G., Brit. 354,992, Sept. 10, 1931; *Cent.* 1931, II 3545. (10) Manchen, Schmidt (to I.G.), Ger. 730,428, May 6, 1943; *C.A.* 38, 2068 (1944); *U.S.* 2,314,454, March 23, 1943; *C.A.* 37, 5078 (1943).

(11) Seidenfaden, Bröcker (to I.G.), Ger. 725,528, Aug. 13, 1942; *C.A.* 37, 5985 (1943). (12) Smorgonskii, Goldfarb, *J. Gen. Chem. (U.S.S.R.)* 10, 1113–1119 (1940); *C.A.* 35, 4011 (1941).

3:9175 *d,l*-4-CHLOROBUTANOL-2  
(1-Chlorobutanol-3)



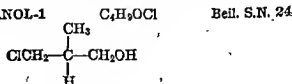
B.P. 70° at 13 mm. (1)

[For prepn. from 3-chloropropanal-1 ( $\beta$ -chloropropionaldehyde) (3:5576) +  $\text{CH}_3\text{MgI}$  see (1) (2).]

[4-Phthalimidobutanol-2, cryst. from pet. eth., m.p. 47–48°, although never recorded by reactn. of  $\bar{\text{C}}$  with *K* phthalimide, has been prepd. indirectly (3).]

3:9175 (1) Fourneau, Ramart-Lucas, *Bull. soc. chim.* (4) 25, 367 (1919). (2) Backer, Bilt, *Rec. trav. chim.* 54, 69–70 (1935). (3) Robinson, Sugimoto, *J. Chem. Soc.* 1932, 308.

3:9180 3-CHLORO-2-METHYLPROPANOL-1



B.P. 76–78° at 21 mm. (1)

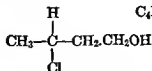
$D_4^{25} = 1.083$  (1)  $n_D^{25} = 1.4460$  (1)

$\bar{C}$  with  $\text{SOCl}_2$  + pyridine gives (1) 1,2-dichlorobutane (3:7680), b.p.  $127^\circ$ ,  $n_D^{25} = 1.4420$  (1).

- $\beta$ -Chloro-*n*-butyl acetate: unreported.
- $\beta$ -Chloro-*n*-butyl benzoate: unreported.
- $\beta$ -Chloro-*n*-butyl *p*-nitrobenzoate: unreported.
- $\beta$ -Chloro-*n*-butyl 3,5-dinitrobenzoate: unreported.
- ⑤  $\beta$ -Chloro-*n*-butyl *N*-phenylcarbamate: m.p.  $52.5$ – $53.5^\circ$  (1).
- 2-(*N*-Phthalimino)butanol-1: unreported.

3:9160 (1) Waddle, Adkins, *J. Am. Chem. Soc.* **61**, 3363 (1939).

3:9165 3-CHLOROBUTANOL-1  
( $\gamma$ -Chloro-*n*-butyl alcohol)



$\text{C}_4\text{H}_9\text{OCl}$

Beil. S.N. 24

B.P.  $67$ – $68^\circ$  at 15 mm. (1)  
 $61^\circ$  at 10 mm. (2)

$D_4^{20} = 1.06218$  (1)  $n_D^{20} = 1.44464$  (1)

$\bar{C}$  on distn. at atm. press. or on htg. with quinoline loses  $\text{HCl}$  and yields crotonyl alc.  $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}_2\text{OH}$ , b.p.  $120$ – $121^\circ$  at 755 mm.,  $D_4^{20} = 0.85306$ ,  $n_D^{20} = 1.42976$  (*N*-phenylcarbamate, m.p.  $79.4$ – $80^\circ$ ) (1).

[For prepn. of  $\bar{C}$  from butanediol-1,3 (1:6482) +  $\text{HCl}$  see (1) (3); from  $\gamma$ -chloro-*n*-butyl butyrate by hydrol. with  $\text{HCl}$  see (2); from  $\text{C}_3\text{H}_6$  + 30%  $\text{CH}_2\text{O}$  +  $\text{HCl}$  at  $50^\circ$  see (4).]

[ $\bar{C}$  over  $\text{Al}_2\text{O}_3$  at  $250^\circ$  gives (3) butadiene-1,3.]

- $\gamma$ -Chloro-*n*-butyl acetate: unreported.
- $\gamma$ -Chloro-*n*-butyl benzoate: unreported.
- $\gamma$ -Chloro-*n*-butyl *p*-nitrobenzoate: unreported.
- $\gamma$ -Chloro-*n*-butyl 3,5-dinitrobenzoate: unreported.
- $\gamma$ -Chloro-*n*-butyl *N*-phenylcarbamate: unreported.
- 3-(*N*-Phthalimino)butanol-1: unreported.

3:9165 (1) Verhulst, *Bull. soc. chim. Belg* **40**, 85–90 (1931). (2) Heyse (to I.G.), Ger. 524,435, May 7, 1931; *Cent* 1931, II 767. (3) Runge, Muller-Cunradi (to I.G.), Ger. 578,038, June 12, 1933, *Cent* 1933, II 935. (4) I.G., Brit. 465,467, June 3, 1937, *Cent* 1937, II 1445.

3:9170 4-CHLOROBUTANOL-1  
( $\delta$ -Chloro-*n*-butyl alcohol;  
tetramethylene chlorohydrin)



$\text{C}_4\text{H}_9\text{OCl}$

Beil. I —

I<sub>1</sub>—

I<sub>2</sub>-(398)

B.P.  $84$ – $85^\circ$  at 16 mm. (1)

$D_4^{25} = 1.125$  (5)

$n_D^{25} = 1.4551$  (5)

$86^\circ$  at 15 mm. (2)

$D_4^{20} = 1.0883$  (1)

$n_D^{20} = 1.4518$  (1)

$81$ – $82^\circ$  at 14 mm. (3) (4)

1.0867 (8)

1.4529 (8)

$72$ – $75^\circ$  at 10 mm. (5)

$70$ – $71^\circ$  at 7 mm. (4)

$64$ – $65^\circ$  at 3 mm. (6)

$57^\circ$  at 0.5 mm. (7)

Colorless liq. — On distn. above 16 mm. splits off  $\text{HCl}$  (1) (2) yielding tetrahydrofuran, b.p.  $63^\circ$ .

[For prepn. from tetrahydrofuran [Beil. XVII-10] by actn. of  $\text{HCl}$  gas (yield; 54–57%

3:9190 *d,l*-3-CHLORO-2-METHYLPROPANEDIOL-1,2  $C_4H_9O_2Cl$  Beil. S.N. 30  
( $\beta$ -Methylglycerol- $\alpha$ -monochlorohydrin)



B.P. 80° at 1.6 mm. (1)

$D_4^{20} = 1.2362$  (1)  $n_D^{20} = 1.4748$  (1)

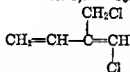
Colorless viscous liq., misc. in all proportions with aq., alc., ether (1).

[For prepn. of  $\bar{C}$  from 1-chloro-2-methyl-2,3-epoxypropane ("  $\beta$ -methylpiclorohydrin " ) (3:7657) by warming with 0.1% aq.  $H_2SO_4$  (95% yield (1)) see (1) (2).]

$\bar{C}$  with aq. 15% NaOH at 10-20° reacts very rapidly (by loss of HCl and ring closure) giving (70% yield (1)) (3) by ether extraction 2,3-epoxy-2-methylpropanol-1 ( $\beta$ -methylglycidol), colorless liq. misc. with aq., alc., or ether, h.p. 68° at 25 mm.,  $D_4^{20} = 1.0420$ ,  $n_D^{20} = 1.4299$  (1). [This prod. on further hydration in the aq. soln. yields 2-methylpropanetriol-1,2,3 ( $\beta$ -methylglycerol), h.p. 115-120° at 1.6 mm.,  $D_4^{20} = 1.1863$ ,  $n_D^{20} = 1.4730$  (1).]

3:9190 (1) Hearne, DeJong, *Ind. Eng. Chem.* **33**, 940-943 (1941). (2) Groll, Hearne (to Shell Development Co.), U.S. 2,086,077, July 6, 1937; *Cent.* 1937, II 2433; *C.A.* **31**, 5813 (1937). (3) Groll, Hearne (to Shell Development Co.), U.S. 2,070,990, Feb. 16, 1937; *Cent.* 1937, II 2433; *C.A.* **31**, 2612 (1937).

3:9195 1-CHLORO-2-(CHLOROMETHYL)BUTADIENE-1,3  $C_6H_7Cl_2$  Beil. I—



I<sub>1</sub>—  
I<sub>2</sub>—

No physical constants on  $\bar{C}$  are cited by the abstract journals.

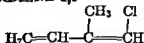
[For formn. of  $\bar{C}$  from 2-(chloromethyl)-1,2,3-trichlorobutane (3:5230) with hqilg. alc. KOH (2-(chloromethyl)-1,3-dichlorobutene-1 (3:9201) is also formed) see (1).]

$\bar{C}$  readily polymerizes (1).

$\bar{C}$  with maleic anhydride (1:0625) forms addn. prods. (1).

3:9195 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **6**, 1116-1132 (1936); *Cent.* 1937, I 573; *C.A.* **31**, 1003 (1937).

3:9200 1-CHLORO-2-METHYLBUTADIENE-1,3  $C_6H_7Cl$  Beil. S.N. 12  
(“ Isoprene monochloride ”)



B.P. 50.4° at 100 mm. (1)

$D_4^{20} = 0.9710$  (1)  $n_D^{20} = 1.4792$  (1)

$\bar{C}$  has pleasant odor resembling isoprene.

[For prepn. of  $\bar{C}$  (38% yield (1) together with other products) from 2-methylbutadiene-1,3 (isoprene) with  $Cl_2$  in  $CCl_4$  see (1); for formn. of  $\bar{C}$  (30% yield (2) together with other products) from 1,2,3-trichloro-2-methylbutane (3:6100) with 2 moles of quinoline at 185-225° see (2).]

$\bar{C}$  with 4 pts. liq.  $SO_2$  gives (1) 1-chloro-2-methylbutene-2 1,4-sulfone, white rhombic plates from water (which effectively separates the accompanying tar), or from ether, m.p. 73° cor. (1). [This prod. is a potent sternutator and skin irritant; its soly. in aq. is about

[For prepn. (76% yield (1)) via hydrolysis of the corresp. trichloroacetate (obtd. by chlorination of isobutyl trichloroacetate) see (1).]

④  $\beta$ -Chloro- $\alpha$ -methyl-*n*-propyl *N*-phenylcarbamate: m.p. 63.5-64° (1).

3:9180 (1) Waddle, Adkins, *J. Am. Chem. Soc.* 61, 3363 (1939).

3:9185 2-( $\beta$ -CHLOROETHOXY)ETHANOL-1  $\text{C}_4\text{H}_9\text{O}_2\text{Cl}$  Beil. I - 467  
(Diethylene glycol chlorohydrin;  $\text{CH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_2\text{OH}$  I<sub>1</sub>—  
ethylene glycol mono- $\beta$ -chloroethyl  $\text{Cl}$  I<sub>2</sub>-(519)  
ether;  $\beta$ -chloroethyl  $\beta$ -hydroxyethyl  
ether;  $\beta$ -chloro- $\beta'$ -hydroxydiethyl ether)

B.P. 180-185° (1)

92-100° at 12 mm. (2)

93-96° at 11 mm. (3)

Colorless mobile highly refractive liq. — Very sol. aq. but can be salted out by addition of  $\text{K}_2\text{CO}_3$ . — Misc. with alc. or ether. [For study of toxicity see (11).]

[For prepn. of  $\bar{\text{C}}$  from ethylene chlorohydrin (3:5552) with ethylene oxide (1:6105) at 140° (4) in pres. of  $\text{SnCl}_4$ ,  $\text{AlCl}_3$ , etc. (2), or acidified hydrosilicate cat. (3), or conc.  $\text{H}_2\text{SO}_4$  (30-35% yield (5)) (together with numerous other prods.), or with ethylene glycol (1:6465) +  $\text{HCl}$  gas as directed (1) see indic. refs.; for prepn. from ethylene oxide (1:6105) satd. with  $\text{HCl}$  gas see (4); for formn. of  $\bar{\text{C}}$  during extractn. of lignin from pine wood by means of ethylene chlorohydrin +  $\text{HCl}$  see (6).]

[For use of quat. salts obtd. from  $\bar{\text{C}}$  by treatment with oleic acid followed by pyridine or from  $\bar{\text{C}}$  with *n*-octadecylamine followed by pyridine and chloroacetic acid see (7); for use of  $\bar{\text{C}}$  as rat poison see (8).]

[ $\bar{\text{C}}$  with hot aq. alk. ring-closes with loss of  $\text{HCl}$  giving (90-95% yield (9)) 1,4-dioxane (1:6400).]

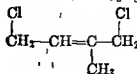
[ $\bar{\text{C}}$  (1 mole) with  $\text{Me}_2\text{NH}$  (3 moles) in  $\text{C}_6\text{H}_6$  in e.t. at 120° for 8 hrs. gives (75% yield (5)) 2-( $\beta$ -dimethylaminoethoxy)ethanol-1, b.p. 95° at 15 mm. ( $\bar{\text{B}}$ .picrolonate, m.p. 110°;  $\bar{\text{B}}$ .*m*-nitrobenzoate. $\text{HCl}$ , m.p. 142°) (5).]

— 2-( $\beta$ -Chloroethoxy)ethyl acetate: oil, b.p. 94-95° at 11 mm. (6).

— 2-( $\beta$ -Chloroethoxy)ethyl *p*-toluenesulfonate: oil; const. not reported. [From  $\bar{\text{C}}$  (1 mole) with *p*-toluenesulfonyl chloride (0.75 mole) at 142° for 10 hrs. (yield 59% (10)); for use in introduction of 2-( $\beta$ -chloroethoxyethyl) group see (10).]

3:9185 (1) Lourenco, *Ann. chim.* (3) 67, 290-292 (1863). (2) Haussmann, Götz, *Ger.* 670,419, Jan. 18, 1939; *Cent.* 1939, II 560; *C.A.* 33, 3031 (1939). (3) I.G., *Brit.* 354,357, Sept. 3, 1931; *Cent.* 1931, II 2657; *C.A.* 26, 3885 (1932). (4) Wurtz, *Ann. chim.* (3) 69, 338-341 (1863). (5) Fourneau, Ribas, *Bull. soc. chim.* (4) 41, 1046-1051 (1927). (6) Freudenberg, Acker, *Ber.* 74, 1406 (1941). (7) I.G., *Brit.* 474,671, Dec. 2, 1937; *Cent.* 1938, 2063, *C.A.* 32, 3518 (1938); French 819,000, Oct. 7, 1937; *Cent.* 1938, 2063; *C.A.* 32, 2653 (1938). (8) I.G., *Brit.* 474,677, Dec. 2, 1937; *Cent.* 1938, I 2045; *C.A.* 32, 3064 (1938). French 805,557, Nov. 24, 1936; *Cent.* 1937, I 3397; *C.A.* 31, 4417 (1937). (9) Webel (to I.G.), *Ger.* 520,478, Oct. 8, 1932; *Cent.* 1933, I 1019; *C.A.* 27, 737 (1933). (10) Butler, Rensfrew, Cretcher, Souther, *J. Am. Chem. Soc.* 59, 228-229 (1937).

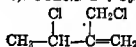
(11) Smyth, Carpenter, *J. Ind. Hyg. Toxicol.* 26, 269-273 (1944).

3:9204 1,4-DICHLORO-2-METHYLBUTENE-2  $C_4H_6Cl_2$  Beil. S.N. 11

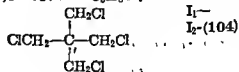
B.P. 93° at 50 mm. (1)

 $D_4^{20} = 1.1526$  (1)  $n_D^{20} = 1.4932$  (1)

56° at 10 mm. (1)

Colorless lachrymatory liquid. — Sol. in cold conc.  $H_2SO_4$  with yel.-br. color.[For prepn. from 2-methylbutadiene-1,3 (isoprene) (1:8020) in  $CCl_4$  by treatment with  $Cl_2$  see (1) (1-chloro-2-methylbutadiene-1,3 (3:9200) is also formed (1)).] $\bar{C}$  in alc. added dropwise to a suspension of Zn dust in hot alc. gives (77% yield (1)) 2-methylbutadiene-1,3 (isoprene) (1:8020), b.p. 34°. $\bar{C}$  on oxidn. with  $KMnO_4$  in acetone at -5° gives (1) 1,4-dichloro-2-methylbutanediol-2,3, ndls. from ether, m.p. 106.5° cor. (1). $\bar{C}$  in  $CHCl_3$  treated with  $O_3$ , then with aq., yields (1) chloroacetone (3:5425) and chloroacetaldehyde (3:7212); ozonolysis of  $\bar{C}$  without solvent followed by  $KMnO_4$  oxidn. gives (1) chloroacetic acid (3:1370).3:9204 (1) Jones, Williams, *J. Chem. Soc.* 1934, 829-834.3:9206 d,l-3-CHLORO-2-(CHLOROMETHYL)BUTENE-1  $C_4H_7Cl_2$  Beil. S.N. 11

"B.P. 39-40° at 7 mm. (1)

 $D_4^{18} = 1.1328$  (1)  $n_D^{18} = 1.4713$  (1)[For formn. of  $\bar{C}$  from 3-chloro-2-methylbutene-1 (3:7300) with  $Cl_2 + NaHCO_3$  at 0° see (1) (yield of  $\bar{C}$  is 35% accompanied by 30% 1,3-dichloro-2-methylbutene-2 (3:8170) and 30% 1,2,3-trichloro-2-methylbutane (3:6100)) (1).] $\bar{C}$  upon ozonolysis yields (1) 1,3-dichlorobutanone-2 (3:5900).3:9206 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, 11 4223; *C.A.* 33, 4190 (1939).— 1,3-DICHLORO-2,2-bis-(CHLOROMETHYL)PROPANE  $C_4H_6Cl_4$  Beil. I - 141

B.P. 110° at 12 mm.

M.P. 97°

See 3:2675. Division A: Solids.

3:9214 2-(CHLOROMETHYL)BUTENE-1  $C_4H_7Cl$  Beil. I - 211  
( $\beta$ -Ethylallyl chloride) $I_1 -$   
 $I_2 - (187)$  $\bar{C}$  has not been obtd. in pure form.[For formn. of  $\bar{C}$  together with 1-chloro-2-methylbutene-1 (3:7303) + 1-chloro-2-methylbutene-2 (3:7485) from 1-chloro-2-methylbutanol-2 (3:8175) by distn. with anhydrous

2.4 g. at 15° and 7.2 g. per 100 ml. aq.; in boilg. aq. it gives a tar, and aq. solns. are therefore concd. under reduced press.; on htg. to 140° under 100 mm. press. it regenerates (77% yield)  $\bar{C}$  and thus constitutes a convenient means for storing  $\bar{C}$  in stable form. (1).]

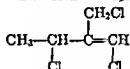
$\bar{C}$  polymerizes at a rate comparable to that of isoprene (for details see (1)).

$\bar{C}$  (6 g.) + 1,4-naphthoquinone (1:9040) (3.5 g.) htd. under  $N_2$  for 4 hrs. at 80° gives (1) on cooling 1-chloro-2-methyltetrahydroanthraquinone, pale yel. ndls. from acetone, colorless ndls. from alc., m.p. 146° cor. (1); this prod. on oxidn. with air in alc. NaOH yields 1-chloro-2-methylanthraquinone, cryst. from AcOH or alc., m.p. 171-172° cor. (1) (3) [dif. from 3-chloropentadiene-1,3 (3:7360) q.v.].

$\bar{C}$  with maleic anhydride (1:0625) evolves HCl and yields (2) a dianhydride.

3:9200 (1) Jones, Williams, *J. Chem. Soc.* 1934, 829-835. (2) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 6, 1116-1132 (1936); *Cent.* 1937, I 573, *C.A.* 31, 1003 (1937). (3) Keimatsu, Hirano, *J. Pharm. Soc. Japan*, 49, 140-147 (1929), *C.A.* 23, 3466 (1929).

3:9201 2-(CHLOROMETHYL)-1,3-DICHLOROBUTENE-1  $C_4H_5Cl_3$  Beil. S.N. 11



B.P. 77-84° at 15 mm. (1)

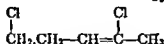
$D_4^{12} = 1.33$  (1)  $n_D^{12} = 1.4075$  (1)

[For prepn. of  $\bar{C}$  from 2-(chloromethyl)1,2,3-trichlorobutane (3:5230) by loss of HCl with boilg. alc. KOH (1-chloro-2-(chloromethyl)butadiene-1,3 (3:9195) is also formed) see (2); for formn. of  $\bar{C}$  from 3-chloro-2-(chloromethyl)butene-1 (3:9206) with  $Cl_2 + NaHCO_3$  at 0° (yield 6%  $\bar{C}$  together with 90% 2-(chloromethyl)-1,2,3-trichlorobutane (3:5230)) see (1).]

$\bar{C}$  on ozonolysis yields (2) 1,3-dichlorobutanone-2 (3:5900) and formic acid (1:1005).

3:9201 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, II 4223; *C.A.* 33, 4190 (1939). (2) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 6, 1116-1132 (1936); *Cent.* 1937, I 573; *C.A.* 31, 1003 (1937)

3:9202 2,5-DICHLOROPENTENE-2  $C_5H_7Cl_2$  Beil. S.N. 11



B.P. 40-41° at 8 mm. (1)

$D_4^{14.5} = 1.1182$  (1)  $n_D^{14.5} = 1.4083$  (1)

[For prepn. of  $\bar{C}$  (92% yield (1)) from cyclopropyl methyl ketone [Beil. VII-7, VII-(5)] with  $PCl_4$  below 20° see (1); for formn. of  $\bar{C}$  from 5-chloropentanone-2 (see below) with excess 50% KOH see (1).]

$\bar{C}$  with conc.  $H_2SO_4$  gives (43% yield (1)) 5-chloropentanone-2 (3:9267).

$\bar{C}$  cannot be hydrolyzed with aq. +  $CaCO_3$  but on protracted reflux (210 hrs.) with excess KOAc in abs. alc. gives 2-chloro-5-acetoxypentene-2, b.p. 81.5° at 13 mm.,  $D_4^{15} = 1.0800$ ,  $n_D^{15} = 1.4499$  (1).

$\bar{C}$  on oxidn. with 3%  $KMnO_4$  gives (1) acetic acid (1:1010) and acrylic acid (1:1020).

$\bar{C}$  on ozonolysis yields (1)  $\beta$ -chloropropionic acid (3:0460).

3:9202 (1) D'yakov, *J. Gen. Chem. (U.S.S.R.)* 10, 414-412 (1940); *C.A.* 34, 7861 (1940).

With alc. NaOEt.  $\bar{C}$  with EtOH/NaOEt yields (23)  $CHCl_3$  (3:5050) + ethyl formate (1:3000).]

With alc. KCN.  $\bar{C}$  with EtOH/KCN gives within 1 min. (88% yield (24)) ethyl dichloroacetate (3:5850): cf. behavior of chloral (3:5210) with KCN in various alcohols.]

With acid chlorides.  $\bar{C}$  with  $AcCl$  (3:7065) gives (25) the corresp. acetate [Beil. I-153], b.p.  $198^\circ$ . —  $\bar{C}$  with isovaleryl chloride (3:7560) gives (41% yield (26)) the corresp. isovalerate, b.p.  $143^\circ$  at 20 mm. (26).]

With diazomethane.  $\bar{C}$  with  $CH_2N_2$  in EtOH soln. at  $0^\circ$  gives (27) trichloroacetaldehyde ethyl-methyl-acetal [Beil. I-621, I<sub>2</sub>-(631)], b.p.  $193.4^\circ$  cor. (28),  $78-80^\circ$  at 13 mm. (27) accompanied by 3,3,3-trichloro-1,2-epoxypropane (3:5760).]

Ⓐ Behavior on heating. Note that  $\bar{C}$  on hfg. gives off inflammable vapor (EtOH) (dif. from chloral hydrate (3:1270) whose initial ignition cannot be maintained).

Ⓑ Behavior with conc.  $HNO_3$ .  $\bar{C}$  reacts violently on warming with conc.  $HNO_3$  (dif. from chloral hydrate (3:1270) which is almost unaffected).

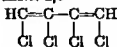
Ⓒ Iodoform test.  $\bar{C}$  with aq. alk. +  $I_2/KI$  soln. on warming gives iodoform, m.p.  $119^\circ$  accompanied of course by  $CHCl_3$  (3:5050) (dif. from chloral hydrate (3:1270)).

3:0869 (1) Jacobsen, *Ann.* 157, 244-245 (1871). (2) Willcox, Brunel, *J. Am. Chem. Soc.* 33, 1821-1841 (1910). (3) Kuntze, *Arch. Pharm.* 246, 98 (1908). (4) Post, *J. Org. Chem.* 6, 830-835 (1941). (5) Leopold, *Z. physik. Chem.* 66, 359-380 (1909). (6) Trillat, *Bull. soc. chim.* (3) 17, 233-234 (1907). (7) Lieben, *Ber.* 3, 909-910 (1870). (8) Nagai, *Biochem. Z.* 152, 263 (1924). (9) Martius, Mendelssohn-Bartholdy, *Ber.* 3, 444 (1879). (10) Kuroakow, Efremov, *Z. physik. Chem.* 85, 411-418 (1913).

(11) Magnani, McElval, *J. Am. Chem. Soc.* 60, 2212 (1938). (12) Personne, *Compt. rend.* 69, 1303 (1899). (13) Crabowsky, Herold, *Z. physik. Chem.* B-28, 290-302 (1935). (14) Buttmann, *Z. physik. Chem.* B-23, 100-104 (1933). (15) Chattaway, Backeberg, *J. Chem. Soc.* 125, 1997-1101 (1924). (16) Bruner, *Cent.* 1902, 1 978. (17) Beckmann, *Z. physik. Chem.* 2, 724-728 (1888). (18) Willcox, Brunel, *J. Am. Chem. Soc.* 33, 2533-2535 (1916). (19) Bynasson, *Bull. soc. chim.* (2) 32, 304 (1879); *Compt. rend.* 87, 26 (1878). (20) Neher, Foster, *J. Am. Chem. Soc.* 31, 410-412 (1909).

(21) Paterno, Pisati, *Gazz. chim. ital.* 2, 333-338 (1872). (22) Henry, *Ber.* 4, 191, 435-438 (1871). (23) Kekulé, *Ann.* 119, 189-189 (1861). (24) Chattaway, Irving, *J. Chem. Soc.* 1929, 1042. (25) Meyer, Dulk, *Ann.* 171, 69-72 (1874). (26) Fourneau, Florence, *Bull. soc. chim.* (4) 47, 353 (1930). (27) Meerweil, Bersin, Burneleit, *Ber.* 62, 1002, 1007-1009 (1929). (28) Magnanni, *Gazz. chim. ital.* 19, 331 (1886). (29) Adams, *J. Pharmacol.* 78, 340-345 (1913); *C.A.* 37, 6035 (1943).

3:0870 1,2,3,4-TETRACHLOROBUTADIENE-1,3  $C_4H_2Cl_4$  Bell. S.N. 12  
(Solid stereoisomer)



M.P.  $50^\circ$  (1)

[See also the liquid stereoisomer (3:6150).]

[For isolation of  $\bar{C}$  from the high-boilg. fractn. resulting in the preparation of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1).]

$\bar{C}$  adds  $Cl_2$  (although much more slowly than its liquid stereoisomer) yielding 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), m.p.  $80^\circ$  (1). [This product with Zn/Cu couple in hot alc. regenerates  $\bar{C}$ , but in alc. with  $Ca(OH)_2$  or with alk. at room temp. gives the liquid stereoisomer (3:9046) (1).]

$\bar{C}$  in  $CHCl_3$  treated with  $Br_2$  gives (100% yield (1)) 1,2-dibromo-1,2,3,4-tetrachlorobutene-2, m.p.  $105^\circ$  (1). [This prod. with Zn/Cu couple in hot alc. regenerates  $\bar{C}$  (1).]

3:0870 (1) Müller, Hüther, *Ber.* 64, 589-600 (1931); *C.A.* 25, 3956 (1931).

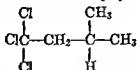
oxalic acid see (1); for formn. of  $\bar{C}$  (together with other products) from 2-methylbutene-1 (1:8210) by actn. of  $Cl_2$  see (2).]

[For behavior of  $\bar{C}$  with NaI in acetone see (2); for use in prepn. of unsatd. cellulose ethers see (3).]

$\bar{C}$  with  $O_3$  followed by hydrolysis yields (2) chloromethyl ethyl ketone (3:8012).

3:9214 (1) Chalmers, *Trans. Roy. Soc. Can.* (3) 22, III 73, 76 (1928). (2) Gutner, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1062-1067 (1938), *Cent.* 1939, II 4221; *C.A.* 33, 3755 (1939). (3) Hahn (to du Pont), U.S. 2,082,797, June 8, 1937; *Cent.* 1937, II 3838; *C.A.* 31, 5577 (1937).

3:9216 4,4,4-TRICHLORO-2-METHYLBUTANE  $C_4H_7Cl_3$  Beil. I-136  
("Isobutylchloroform")



I<sub>1</sub>—  
I<sub>2</sub>—

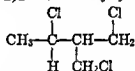
No physical constants of  $\bar{C}$  have been reported.

[For formn. of  $\bar{C}$  from diisooamyl sulfide [Beil. I-405, I<sub>1</sub>-(200), I<sub>2</sub>-(435)] by action of  $Cl_2$  see (1).]

$\bar{C}$  on htg. in a s.t. for 5 hrs. at 110° with  $Ag_2O$  + aq. yields (1) isovaleric acid (1:1050).

3:9216 (1) Spring, Lecrenier, *Bull. soc. chim.* (2) 48, 627 (1887).

3:9218 d,l-1,3-DICHLORO-2-(CHLOROMETHYL)BUTANE  $C_4H_7Cl_3$  Beil. S.N. 10



B.P. 79-81° at 15 mm. (1)

$D_4^{15} = 1.2793$  (1)

$n_D^{15} = 1.4899$  (1)

$n_D^{15} = 1.4970$  (1)

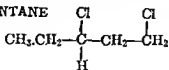
[For formn. of  $\bar{C}$  from 1,3-dichloro-2-methylbutane (3:9228) or from 3-chloro-2-methylbutene-1 (3:7300) with  $Cl_2$  see (1).]

$\bar{C}$  with  $Cl_2$  as specified (1) yields 1,2,3-trichloro-(2-chloromethyl)butane (3:5230).

$\bar{C}$  with KOH or with quinoline gives (1) only resins.

3:9218 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 6, 1116-1132 (1936); *Cent.* 1937, I 573; *C.A.* 31, 1003 (1937).

3:9220 d,l-1,3-DICHLOROPENTANE  $C_5H_9Cl_2$  Beil. S.N. 10



B.P. 80.4° at 60 mm. (1)

$D_4^{20} = 1.0834$  (1)

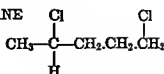
$n_D^{20} = 1.4485$  (1)

[For prepn. of  $\bar{C}$  (30% yield (1) together with other products) from 1-chloropentane (3:7460) by vapor-phase photochemical chlorination see (1).]

$\bar{C}$  on refluxing 24 hrs. with NaI in acetone gives (90% yield (1)) 3-chloro-1-iodopentane, b.p. 50.5° at 2.5 mm.,  $D_4^{20} = 1.6611$ ,  $n_D^{20} = 1.5229$  (1). (A small amt. of 1,3-diiodopentane, b.p. 80-82° at 2.5 mm., is also formed (1).) [For reactn. of 3-chloro-1-iodopentane with diethylamine to give (74% yield) 3-chloropentyl-diethylamine HCl, m.p. 98.5°, see (1).]

3:9220 (1) Hlass, Huffman, *J. Am. Chem. Soc.* 63, 1233-1235 (1941).



3:9224 *d,l*-1,4-DICHLOROPENTANE $\text{C}_5\text{H}_{10}\text{Cl}_2$  Beil. I-131I<sub>1</sub>—I<sub>2</sub>—

B.P. 88.1° at 60 mm. (1)

69-70° at 28 mm. (3)

59-61° at 17 mm. (2)

58-60° at 15 mm. (2)

 $D_4^{20} = 1.0840$  (1)  $n_D^{20} = 1.4503$  (1)

[For prepn. of  $\bar{\text{C}}$  (31% yield (1) together with other prods.) from 1-chloropentane (3:7460) by vapor-phase photochemical chlorination see (1); from 2-methyltetrahydrofuran [Beil. XVII-12] on htg. in a.t. for 4 hrs. at 60° with 2 vols. conc. HCl (2) or from pentanediol-1,4 by treatment in boilg. aq. with HCl (2) see indic. refs. — For formn. of  $\bar{\text{C}}$  (together with other prods.) from pentane (1:8505) +  $\text{Cl}_2$  see (3).]

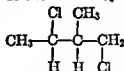
$\bar{\text{C}}$  on boilg. with aq. (2) or aq.  $\text{K}_2\text{CO}_3$  (3) yields pentanediol-1,4 [Beil. I-480] [*bis*-(*N*-phenylcarbamate), m.p. 125-125.5° (3)].

$\bar{\text{C}}$  on refluxing 24 hrs. with NaI in acetone gives (90% yield (1)) 4-chloro-1-iodopentane, b.p. 61.3° at 3.5 mm.,  $D_4^{20} = 1.6580$ ,  $n_D^{20} = 1.5248$  (1) (a small amt. of 1,4-diiodopentane, b.p. 100° at 5 mm. is also formed (1)). [For reactn. of 4-chloro-iodopentane with diethylamine to give (42% yield) 4-chloropentyl-diethylamine hydrochloride, m.p. 99°, see (1).]

3:9224 (1) Hass, Huffman, *J. Am. Chem. Soc.* **63**, 1233-1235 (1941). (2) Fröbe, Hochstetter, *Monatsh.* **23**, 1087-1088 (1902). (3) Lemke, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **7**, 1995-1998 (1937); *Cent.* 1939, I 2398; *C.A.* **32**, 482 (1938).

3:9228 *d,l*-1,3-DICHLORO-2-METHYLBUTANE $\text{C}_5\text{H}_{10}\text{Cl}_2$ 

Beil. S.N. 10



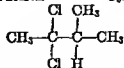
Note that  $\bar{\text{C}}$  has never been reported; the prod. originally supposed by (1) to have been  $\bar{\text{C}}$  was later (2) found to be 2-(chloromethyl)-3-chlorobutene-1 (3:9206) q.v.

By chlorination of opt. act. 1-chloro-2-methylbutane with  $\text{SO}_2\text{Cl}_2$  in pres. of benzoyl peroxide followed by subsequent fractionation (3) both opt. act. forms of  $\bar{\text{C}}$  are alleged to have been obtd.; *dextro* form, b.p. 155° at 760 mm. (calcd.), 91° at 100 mm. (obs.); *levo* form, b.p. 153° at 760 mm. (calcd.), 89.2° at 100 mm. (obs.) (3). Note, however, that in (3) the authors were apparently unaware of the correction mentioned above.

3:9228 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **7**, 1995-1998 (1937); *Cent.* 1939, I 2398; *C.A.* **31**, 1003 (1937). (2) Fröbe, Hochstetter, *Monatsh.* **23**, 1087-1088 (1902). (3) Brown, Kharasch, *J. Am. Chem. Soc.* **63**, 1233-1235 (1941).

3:9230 *d,l*-1,3-DICHLORO-2-METHYLBUTANE $\text{C}_5\text{H}_{10}\text{Cl}_2$ 

Beil. I-135

I<sub>1</sub>—I<sub>2</sub>—

No data on physical properties of  $\bar{\text{C}}$  appear to be recorded.

[For prepn. of  $\bar{\text{C}}$  from isopropyl methyl ketone (1:5410) with  $\text{PCl}_5$  see (1).]

$\bar{\text{C}}$  with alc. KOH at 130° yields (1) isopropylacetylene (1:8010), b.p. 28°.

3:9230 (1) Béhal, *Ann. chim.* (6) **15**, 285-286 (1888).

3:9240	TIGLYL CHLORIDE ( <i>cis</i> - $\alpha$ -Methylcrotonoyl chloride; <i>cis</i> - $\alpha,\beta$ -dimethylacryloyl chloride)	$\text{CH}_3\text{C}_6\text{H}_7\text{OCl}$ $\text{CH}_3\text{C}(\text{Cl})=\text{C}=\text{O}$	Beil. II - 431 II <sub>1</sub> — II <sub>2</sub> —
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B.P. 64° at 35 mm. (1)

45° at 12 mm. (2)

[For prepn. of  $\bar{\text{C}}$  from tiglic acid (1:0420) with  $\text{PCl}_3$  (yield 90% (1)) (2) see indic. refs.]  
 $\bar{\text{C}}$  with hydrazine hydrate (2 moles) yields (3) *N,N'*-ditiglylhydrazide, m.p. 182–183° (3).  
 $\bar{\text{C}}$  on hydrolysis yields tiglic acid (1:0420), m.p. 64.5–65°, q.v. for the corresp. amide, anilide, *p*-toluidide, and other derivs.]

3:9240 (1) Barger, Martin, Mitchell, *J. Chem. Soc.* 1937, 1822. (2) Blaise, Bagard, *Ann. chim.* (8) 11, 120 (1907). (3) Freri, *Atti X<sup>o</sup> Congr. intern. chim.* 3, 150–154 (1939); *Cent.* 1939, II 3975; *C.A.* 34, 100 (1940).

3:9242	ETHYL $\alpha$ -CHLOROACRYLATE	$\text{C}_6\text{H}_7\text{O}_2\text{Cl}$ $\text{CH}_2=\text{C}(\text{Cl})\text{COOC}_2\text{H}_5$	Beil. S.N. 163
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B.P. 51–53° at 18 mm. (1)

 $n_D^{20} = 1.4384$  (1)

[For prepn. of  $\bar{\text{C}}$  from ethyl  $\alpha,\beta$ -dichloropropionate (3:6090) by htg. with dimethylaniline, quinoline, or quinaldine at 100° for 10 min. under  $\text{N}_2$  (81% yield) see (1).]

See also  $\alpha$ -chloroacrylic acid (3:1445) and methyl  $\alpha$ -chloroacrylate (3:9096).

3:9242 (1) Marvel, Dec, Cooke, Cowan, *J. Am. Chem. Soc.* 62, 3495–3498 (1940).

3:9244	METHYL $\beta$ -CHLOROCROTONATE	$\text{C}_6\text{H}_7\text{O}_2\text{Cl}$ $\text{CH}_3\text{C}(\text{Cl})=\text{C}(\text{H})\text{COOCH}_3$	Beil. II — II <sub>1</sub> -(189) II <sub>2</sub> -(396)
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B.P. 64–67° at 14 mm. (1)

 $D_4^{22.3} = 1.1555$  (1) $D_4^{21.4} = 1.1564$  (1)  $n_D^{21.4} = 1.46275$  (1) $D_4^{20} = 1.157$  (1)

[See also methyl  $\beta$ -chloroisocrotonate (3:8028).]

[For prepn. of  $\bar{\text{C}}$  from  $\beta$ -chlorocrotonic acid (3:2625) in MeOH (1:6120) with dry HCl see (1).]

[ $\bar{\text{C}}$  with Na salt of benzyl mercaptan gives (2) methyl  $\beta$ -(benzylmercapto)crotonate, cryst. from ether and MeOH, m.p. 69–70° (2), 73° (3), also obtd. (78% yield (3)) from Na thioenolate of methyl  $\beta$ -mercaptocrotonate with benzyl chloride (3:8535); note that this (and also other, analogous products) are also obtd. starting with the stereoisomeric methyl  $\beta$ -chloroisocrotonate (3:8028) q.v.]

3:9244 (1) von Auwers, *Ber.* 45, 2806–2807 (1912). (2) Scheibler, Voss, *Ber.* 53, 384 (1920). (3) Scheibler, Topouzada, Schulze, *J. prakt. Chem.* (2) 124, 20 (1940).

**3:9246 ETHYL (CHLOROFORMYL)ACETATE**  
 (Carbethoxyacetyl chloride)


Beil. II - 582

II<sub>1</sub>-(252)II<sub>2</sub>-(529)

B.P. 75-77° at 17 mm. (1)

71° at 15 mm. (2)

68-70° at 13 mm. (3)

63-64° at 10 mm. (4)

See also methyl (chloroformyl)acetate (3:9093-A.)

Note that  $\bar{\text{C}}$  is both an acid chloride and an ester; it comprises the half acid chloride/half ethyl ester of malonic acid (1:0480).

[For prepn. of  $\bar{\text{C}}$  from ethyl hydrogen malonate with  $\text{SOCl}_2$  (3) or better from potassium ethyl malonate with  $\text{SOCl}_2$  at 0° (1) or in ether (4) (yields: 70% (1), 45% (4)) cf. (5) or with  $\text{PCl}_5$  (6) see indic. refs.]

$\bar{\text{C}}$  boils at ord. press. about 170-180° with serious decompn. (3). —  $\bar{\text{C}}$  on repeated distn. even under reduced press. (4) or  $\bar{\text{C}}$  with quinoline in dry ether at 0° (4) loses  $\text{HCl}$  and undergoes condensation yielding ethyl 6-ethoxy-2,4-diketo-2,3-dihydropyran-3-carboxylate [Beil. XVIII<sub>1</sub>-(540)], cryst. from  $\text{CS}_2$ , m.p. 85-86° (4) cf. (7).

[For behavior of  $\bar{\text{C}}$  with 2,4-dimethylpyrrol  $\text{MgBr}$  (8), with indolyl  $\text{MgBr}$  (5), with indolyl  $\text{MgI}$  (9), or with imidazolyl  $\text{MgBr}$  (10) see indic. refs.]

[For behavior of  $\bar{\text{C}}$  with atoxyl see (1).]

$\bar{\text{C}}$  with urea (2 moles) reacts as an acid chloride giving (2) ethyl malonurate (Beil. III-66), m.p. 128° (2). —  $\bar{\text{C}}$  with thioformamide condenses with loss of  $\text{H}_2\text{O} + \text{HCl}$  giving (11) (12) (13) ethyl thiazole-5-carboxylate, h.p. 103.5-104.5° at 12 mm. (13), which on hydrolysis gives thiazole-5-carboxylic acid, m.p. 196-197° cor. (11).]

—  $\omega$ -(Carbethoxyacet)anilide: unreported.

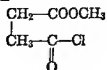
①  $\omega$ -(Carbethoxyacet)-*p*-toluidide: m.p. 83° (4).

3:9246 (1) Morgan, Walton, *J. Chem. Soc.* 1931, 1744-1745. (2) Boehringer und Söhne, Ger. 193,447, Dec. 28, 1907; *Cent.* 1908, I 1000; *C.A.* 2, 1862-1863 (1908). (3) Marguery, *Bull. soc. chim.* (3) 33, 546-547 (1905). (4) Staudinger, Becker, *Ber.* 50, 1023 (1917). (5) Oddo, Albanese, *Gazz. chim. ital.* 57, 833-834 (1927). (6) van't Hoff, *Ber.* 7, 1572 (1874). (7) Leuchs, *Ber.* 39, 2642-2643 (1906). (8) Ingrassia, *Gazz. chim. ital.* 64, 780-782 (1934). (9) Majima, Shigematsu, Rokkaku, *Ber.* 57, 1454-1455 (1924). (10) Oddo, Quintino, *Gazz. chim. ital.* 58, 595-596 (1928).

(11) Erlenmeyer, von Meyenburg, *Helv. Chim. Acta* 20, 205 (1937). (12) Soc. Chem. Ind. Basel, Swiss 192,849, Nov. 16, 1937; *Cent.* 1938, I 3659; *C.A.* 32, 4285 (1938). (13) Soc. Chem. Ind. Basel, Ger. 658,353, March 29, 1938, *Cent.* 1938, II 354; *C.A.* 32, 4727 (1938).

**3:9247 METHYL  $\beta$ -(CHLOROFORMYL)PROPIONATE**  
 ( $\beta$ -Carbomethoxy)propionyl chloride)

Beil. S.N. 172



B.P. 93° at 18 mm. (1) (2)

92-93° at 18 mm. (3)

89-90° at 16 mm. (3)

85-87° at 15 mm. (4)

85.5-87° at 13 mm. (3)

84° at 12 mm. (5)

Note that  $\tilde{C}$  is both an acid chloride and an ester;  $\tilde{C}$  is an important reagent for introducing the three-carbon radical  $-\text{CH}_2\text{CH}_2\text{COOH}$ .

[For prepn. of  $\tilde{C}$  from methyl hydrogen succinate, m.p.  $58^\circ$  (itself ohd. (yields: 95-96% (3), 83% (4) (1) from succinic anhydride (1:0710) with MeOH (1:6120)) by action of  $\text{SOCl}_2$  (yields: 100% (6), 90-93% (3), 90% (5)) or of  $\text{PCl}_5$  (92.5% yield (4)) see indic. refs. Note that  $\tilde{C}$  on distn. (except at low press.) tends to lose MeCl (3:7005) giving (3). succinic anhydride (1:0710).

Examples of utility of  $\tilde{C}$  in synthesis include the following:  $\tilde{C}$  + ethyl sodio-acetoacetate (6);  $\tilde{C}$  + ethyl sodio- $\alpha$ -acetyl-*n*-undecanoate (7);  $\tilde{C}$  + ethyl sodio- $\alpha$ -acetyl- $\gamma$ -phenoxy-*n*-butyrate (8);  $\tilde{C}$  + ethyl sodio- $\gamma$ -phenoxypropylacetoacetate (9);  $\tilde{C}$  + methyl  $\gamma$ -(6-methoxy-1-naphthyl)butyrate (10);  $\tilde{C}$  + methyl sodio- $\alpha$ -acetylpropionate (11);  $\tilde{C}$  + 1-methylcyclohexene-1 (5);  $\tilde{C}$  + ethyl  $\alpha$ -acetyl-*n*-tridecanoate (1);  $\tilde{C}$  + Cd diisoamyl (4).]

—  $\beta$ -(Carbomethoxy)propionamide: unreported.

③  $\beta$ -(Carbomethoxy)propionanilide: ndls. from ether or lt. pet./ $\text{C}_6\text{H}_6$ , m.p.  $97-99^\circ$  (1).

[From  $\tilde{C}$  with aniline (1).]

3:9247 (1) G. M. Robinson, R. Robinson, *J. Chem. Soc.* 127, 180 (1925). (2) Clutterheck, R. Robinson, *Biochem. J.*, 19, 385-396 (1925); *Cent.* 1925, II 1516 (3) Cason, *Org. Syntheses* 25, 19-22 (1945) (4) Cason, *J. Am. Chem. Soc.* 64, 1107 (1942) (5) Nenitzescu, Cioranescu, Przemetzky, *Ber.* 73, 314 (1940). (6) Ruggli, Maeder, *Helv. Chim. Acta* 25, 943 (1942); *C. A.* 37, 1714-1715 (1943). (7) G. Robinson, R. Robinson, *J. Chem. Soc.* 1926, 2206. (8) R. Robinson, Watt, *J. Chem. Soc.* 1934, 1539. (9) Barger, R. Robinson, Smith, *J. Chem. Soc.* 1937, 724. (10) R. Robinson, Thompson, *J. Chem. Soc.* 1938, 2011.

(11) R. Robinson, Seijo, *J. Chem. Soc.* 1941, 585.

3:9250  $\beta$ -METHOXYETHYL TRICHLOROACETATE  $\text{C}_6\text{H}_7\text{O}_2\text{Cl}_3$  Beil. S.N. 160  
(Methyl "cellosolve" trichloroacetate)  $\text{CH}_2\text{OCH}_3$   
 $\text{CH}_2\text{OCOCCL}_3$

B.P.

M.P.

98.0-90.5° at 17 mm. (2) 14.6-14.8° (1)  $D_4^{20} = 1.3866$  (3)  $n_D^{20} = 1.45626$  (2)  
92-93° at 10 mm. (1) 1.3826 (2) 1.45823 (2)  
61° at 0.9 mm. (3)

Colorless liq. with agreeable odor.

[For prepn. (82% yield (1)) from  $\beta$ -methoxyethanol (1:6405) + trichloroacetyl chloride (3:5420) see (1).]

$\tilde{C}$  on shaking with ac. is smoothly saponified (1) to  $\beta$ -methoxyethanol (1:6405) + trichloroacetic ac. (3:1150).

3:9250 (1) Meerwein, Sönke, *Ber.* 64, 2379 (1931). (2) Palomaa, Salmi, Korte, *Ber.* 72, 797 (1939). (3) Meerwein, Sönke, *J. prakt. Chem.* (2) 137, 309 (1933).

3:9260 *d,l*- $\gamma$ -CHLORO-*n*-VALERYL CHLORIDE  $\text{C}_6\text{H}_9\text{OCl}_2$  Beil. II —  
 $\text{CH}_2\text{CH}(\text{Cl})\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{Cl}$  II<sub>1</sub>-(132)  
II<sub>2</sub>—

B.P.  $61^\circ$  at 8 mm. (1)

[For prepn. of  $\tilde{C}$  from  $\gamma$ -chloro-*n*-valeric acid (3:9270) with sl. excess of  $\text{SOCl}_2$  (100% yield) see (1).]

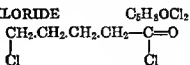
( $\tilde{C}$  with  $\text{EtZnI}$  at  $-15^\circ$  to  $-20^\circ$  yields (2)  $\gamma$ -chloro-*n*-butyl ethyl ketone (6-chlorohexa-

none-3) [Beil. I<sub>1</sub>-(359)], b.p. 79° at 13 mm. (2) (semicarbazone, m.p. 129-129.5° (2), p-nitrophenylhydrazone, unrecryst. oil (2));  $\bar{C}$  with  $C_6H_5ZnBr$  at 0° yields (3)  $\gamma$ -chloro-*n*-butyl phenyl ketone [Beil. VII<sub>1</sub>-(173)], b.p. 155-156° at 15 mm. (3) (semicarbazone, m.p. 123° (3)).]

$\bar{C}$  on hydrolysis with aq. yields (1)  $\gamma$ -chloro-*n*-valeric acid (3:9270); for the amide, anilide, and other derivs. corresp. to  $\bar{C}$  see the acid (3:9270).

3:9260 (1) Wohlge-muth, *Compt. rend.* 159, 80 (1914); *Ann. chim.* (9) 2, 301 (1914). (2) Wohlge-muth, *Ann. chim.* (9) 2, 405-406, 410-412 (1914). (3) Ref. 2, 417-419.

### 3:9264 $\delta$ -CHLORO-*n*-VALERYL CHLORIDE



Beil. S.N. 162

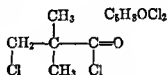
B.P. 75-80° at 5-8 mm. (1)

[For prepn. of  $\bar{C}$  from  $\delta$ -chloro-*n*-valeric acid (3:0075) with  $\text{SOCl}_2$  see (1).]

3:9264 (1) Child, Pyman, *J. Chem. Soc.* 1931, 41.

### 3:9266 CHLOROPIVALYL CHLORIDE

( $\beta$ -Chloro- $\alpha,\alpha$ -dimethylpropionyl chloride)



Beil. S.N. 162

B.P. 85-86° at 60 mm. (1)

$n_D^{20} = 1.4539$  (1)

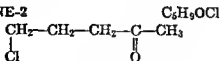
[For prepn. of  $\bar{C}$  from pivalyl chloride (trimethylacetyl chloride) (3:7450) with  $\text{SO}_2\text{Cl}_2$  + dibenzoyl peroxide in  $\text{CCl}_4$  see (1).]

Ⓒ Chloropivalamide: pl. from aq., m.p. 108-109° (1).

3:9266 (1) Kharasch, Brown, *J. Am. Chem. Soc.* 62, 925-929 (1940)

### 3:9267 5-CHLOROPENTANONE-2

( $\gamma$ -Chloro-*n*-propyl methyl ketone)



Beil. I —

I<sub>1</sub>—I<sub>2</sub>-(738)

B.P. 76° at 34 mm. (6)

$D_4^{18} = 1.0571$  (1)

$n_D^{18} = 1.4461$  (1)

74-75° at 23 mm. (1)

$n_D^{18} = 1.4371$  (1)

71-72° at 20 mm. (2)

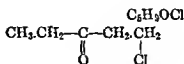
[For prepn. of  $\bar{C}$  from 2,5-dichloropentene-2 (3:9202) by hydration with conc.  $\text{H}_2\text{SO}_4$  (43% yield) see (1); from 2,5-epoxypentene-1 ("α-methylenetetrahydrofuran") (for whose prepn. + characteristics see (3)) by ring cleavage with conc.  $\text{HCl}$  see (4); from cyclopropyl methyl ketone cyanohydrin ("acetyltrimethylene cyanohydrin") with conc.  $\text{HCl}$  by ring cleavage and loss of  $\text{HCN}$  see (5); from α-acetobutyrolactone with  $\text{HCl}$  as directed see (6).]

[ $\bar{C}$  with 50% excess  $\text{KOH}$  on refluxing loses  $\text{HCl}$  and ring-closes giving (60% yield (2)) (5) cyclopropyl methyl ketone [Beil. VII-7, VII<sub>1</sub>-(7)], b.p. 112-113° (5),  $D_4^{20} = 0.8993$ ,  $n_D^{20} = 1.4244$  (corresp. semicarbazone, m.p. 120-121° (5)).]

Ⓒ 5-Chloropentanone semicarbazone: m.p. 92-93° (5), 91-92° (1).

3:9267 (1) D'yakonov, *J. Gen. Chem. (U.S.S.R.)* 10, 414-426 (1940); *C.A.* 34, 7861 (1940).  
 (2) Zelinsky, Dengin, *Ber.* 55, 3360 (1922). (3) Paul, *Bull. soc. chim.* (4) 53, 425-426 (1933);  
 (5) 2, 752-754 (1935). (4) Topchiev, *Russ.* 57,345, June 30, 1940; *C.A.* 36, 2509 (1942). (5)

3:9268 1-CHLOROPENTANONE-3  
 (β-Chloroethyl ethyl ketone)



Beil. I-680

I<sub>1</sub>—  
 I<sub>2</sub>—

B.P. 68° at 20 mm. (1)

48-56° at 13 mm. (2)

57° at 9 mm. (1)

[For prepn. of  $\bar{\text{C}}$  from propionyl chloride (3:7170) with ethylene +  $\text{AlCl}_3$  with or without diluent (50% yield (4)) (2), or over suitable cat. at 100-300° and at 20-200 atm. press. (3), see indic. refs.; from β-chloropropionyl chloride (3:5690) with  $\text{ZnEt}_2$  in toluene (70% yield) see (1).]

$\bar{\text{C}}$  with hot aq. alk. or alk. carbonates gives only resins, but  $\bar{\text{C}}$  on boilg. with dry diethylamine loses  $\text{HCl}$  yielding (1) ethyl vinyl ketone [Beil. I-731, I<sub>2</sub>-(791)], h.p. 96°.

$\bar{\text{C}}$  with diethyl sodio-malonate in ether gives (5) diethyl α-(γ-keto-n-amy)malonate, b.p. 166° at 14 mm. (5);  $\bar{\text{C}}$  with sodio-acetylacetone yields (5) the triketone 3-acetyloctanedione-2,6, h.p. 154° at 16 mm. (5);  $\bar{\text{C}}$  with ethyl sodio-acetoacetate in ether yields (6) the expected ethyl octandione-2,6-carboxylate-3 (3-carbethoxyoctanedione-2,6), h.p. 150° at 8 mm. (6).]

$\bar{\text{C}}$  with diethylamine in ether in cold, followed by treatment with dil. aq. alk., yields (7) 1-diethylaminopentanone-3, b.p. 84° at 13 mm.,  $n_D^{25} = 1.4368$  (7).]

$\bar{\text{C}}$  with aniline (2 moles) + a little water reacts vigorously on warming yielding (3) 1-anilinopentanone-3 [Beil. XII-214], tbs. from ether, m.p. 55.5° (8); note, however, that  $\bar{\text{C}}$  with aniline htd. in abs. alc. or  $\text{C}_6\text{H}_6$  (8), or  $\bar{\text{C}}$  with aniline htd. with conc.  $\text{HCl}$  (or 40%  $\text{H}_2\text{SO}_4$ ) + nitrobenzene (or  $\text{H}_3\text{AsO}_4$ ), gives (9) (4) 4-ethylquinoline [Beil. XX-406, XX-1(153)]].

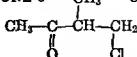
$\bar{\text{C}}$  with hydrazine hydrate in  $\text{MeOH}$  gives (80% yield (10)) by ring closure 3-ethyl-Δ<sup>2</sup>-pyrazoline [Beil. XXIII-32], liq., b.p. 76° at 22 mm. (10) (corresp. picrate,  $\text{B.PkOH}$ , yel. ndls. from 95° alc., m.p. 117° (10)). —  $\bar{\text{C}}$  with phenylhydrazine in ether gives (10) by ring closure 3-ethyl-1-phenyl-Δ<sup>2</sup>-pyrazoline [Beil. XXIII-32], oil, h.p. 155° at 9 mm. (10).]

$\bar{\text{C}}$  with  $\text{NH}_2\text{OH.HCl}$  +  $\text{K}_2\text{CO}_3$  in aq.  $\text{MeOH}$  htd. for a few minutes gives (20% yield (10)) by ring closure 3-ethyl-Δ<sup>2</sup>-isoxazoline [Beil. XXVII-13], oil, b.p. 69° at 11 mm. (10).]

⊕ 1-Carbamido-3-ethyl-Δ<sup>2</sup>-pyrazoline: cryst. from  $\text{EtOAc}$  or  $\text{C}_6\text{H}_6$ , m.p. 96° (10).

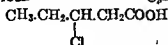
[Note that  $\bar{\text{C}}$  with 1 equiv. semicarbazide  $\text{HCl}$  +  $\text{NaOAc}$  in aq. immediately ppts. the corresp. semicarbazone; this on htg. with strong aq.  $\text{NaOAc}$  (or  $\bar{\text{C}}$  + semicarbazide  $\text{HCl}$  + strong  $\text{NaOAc}$  soln. htd. directly) loses  $\text{HCl}$  and ring-closes to the indic. deriv. (10).]

3:9268 (1) Blaise, Maire, *Bull. soc. chim.* (4) 3, 268-271 (1905); *Compt. rend.* 142, 216 (1906).  
 26, 1929; *Cent.* 1930, II 1133; *Brit.* 282,412,  
 zevich (to Standard Oil Development Co.),  
 (4) Kenner, Statham, *Ber.* 69, 16-17 (1936).  
 905) (6) Blaise, Maire, *Bull. soc. chim.* (4)  
 inson, Simonsen, *J. Chem. Soc.* 1937, 1578,  
 665 (1908) (9) Schering-Kahlbaum, A.G.,  
 (10) Blaise, Maire, *Bull. soc. chim.* (4) 3,  
 272-279 (1905).

3:9269 1-CHLORO-2-METHYLBUTANONE-3  $\text{CH}_3$   $\text{C}_4\text{H}_9\text{OCl}$  Beil. S.N. 87

B.P. 60-62° at 16 mm. (1)

[For prepn. of  $\bar{\text{C}}$  from 2-methylbutanon-3-ol-1 ( $\beta$ -acetyl-*n*-propyl alc.) [Beil. I<sub>1</sub>-(422)] with 3 moles HCl (satd. at 0°), preferably in pres. of 5-10%  $\text{AlCl}_3$  (50% yield, accompanied by some 2-methylbuten-1-one-3, b.p. 96-99°) see (1).]

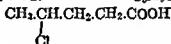
3:9269 (1) Decombe, *Compt. rend.* 202, 1685-1687 (1936); *Cent.* 1936, II 1525.— *d,l*- $\beta$ -CHLORO-*n*-VALERIC ACID  $\text{C}_6\text{H}_9\text{O}_2\text{Cl}$  Beil. S.N. 162

B.P. 112° at 10 mm.

M.P. 33°

 $D_4^{20} = 1.1484$  $n_D^{20} = 1.4462$ 

See 3:0270. Division A: Solids.

3:9270 *d,l*- $\gamma$ -CHLORO-*n*-VALERIC ACID  $\text{C}_6\text{H}_9\text{O}_2\text{Cl}$  Beil. II —II<sub>1</sub>-(131)II<sub>2</sub>—

B.P. 117° at 10 mm. (1)

 $D_4^{20} = 1.1514$  (1) $n_D^{20} = 1.4458$  (1)

115-116° at 10 mm. (2)

1.1510 (1)

1.4450 (1)

[For prepn. of  $\bar{\text{C}}$  from  $\gamma$ -*n*-valerolactone (1:5080) with conc. HCl at 150° see (2); from  $\beta$ -ethylidene-propionic acid (penten-3-oic acid-1) [Beil. II-426, II<sub>1</sub>-(191), II<sub>2</sub>-(400)] or from allyl-acetic acid (penten-4-oic acid-1) [Beil. II-425, II<sub>1</sub>-(191), II<sub>2</sub>-(399)] with dry HCl gas in ether or heptane at -15° see (1).] [For opt. act. isomers of  $\bar{\text{C}}$  see Beil. II<sub>2</sub>-(268) and subsequent literature.]

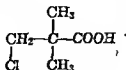
 $\bar{\text{C}}$  with  $\text{SOCl}_2$  yields (2)  $\gamma$ -chloro-*n*-valeryl chloride (3:9260).— Methyl  $\gamma$ -chloro-*n*-valerate: unrecorded.— Ethyl  $\gamma$ -chloro-*n*-valerate: b.p. 196° (see 3:8703).

①  $\gamma$ -Chloro-*n*-valeramide: tpls. from ether, m.p. 79-79.5° (2). [From  $\gamma$ -chloro-*n*-valeryl chloride (3:9260) with conc. aq.  $\text{NH}_4\text{OH}$  (2).]

②  $\gamma$ -Chloro-*n*-valer-anilide: ndls. from pet. eth. + a little AcOH, m.p. 104° (2). [From  $\gamma$ -chloro-*n*-valeryl chloride (3:9260) with aniline in ether soln. (2).]

③  $\gamma$ -Chloro-*n*-valero-phenylhydrazide: ndls. from EtOAc, m.p. 100° (2). [From  $\gamma$ -chloro-*n*-valeryl chloride (3:9260) with 2 moles phenylhydrazine in ether (2).]

3:9270 (1) Schjanberg, *Ber.* 70, 2385-2391 (1937). (2) Wohlgemuth, *Compt. rend.* 158, 1577 (1914); *Ann. chim.* (9) 2, 298-304 (1914).

— CHLOROPIVALIC ACID  $\text{C}_6\text{H}_9\text{O}_2\text{Cl}$  Beil. S.N. 162

B.P. 126-129° at 30 mm.

M.P. 40-42°

See 3:0440. Division A: Solids.

- 3:9280  $\beta$ -ETHOXYETHYL CHLOROFORMATE  $C_5H_9O_3Cl$  Beil. S.N. 199  
 ("Cellosolve" chloroformate;  $C_2H_5O.CH_2.CH_2.O.CO.Cl$   
 $\beta$ -ethoxyethyl chlorocarbonate)

B.P. 67.2° at 14 mm. (1)  $D_{40}^{25} = 1.1341$  (1)  $n_D^{25} = 1.4169$  (1)

Colorless liq. insol. aq.

[For prepn. (77% yield (1)) from  $\beta$ -ethoxyethanol ("Cellosolve") (1:6410) + phosgene (3:5000) see (1).]

⑤  $\beta$ -Ethoxyethyl carhamate: m.p. 62.2° (1). [From  $\bar{C}$  + aq.  $NH_4OH$  in 39% yield; cryst. from propylene chloride (1)]

3:9280 (1) Asburn, Collett, Lazzell, *J. Am. Chem. Soc.* **60**, 2933-2934 (1938).

- 3:9285  $\beta$ -METHOXYETHYL CHLOROACETATE  $C_5H_9O_3Cl$  Beil. S.N. 160  
 (Methyl "cellosolve" chloroacetate)  $CH_2.O.CH_3$   
 $|$   
 $CH_2.O.CO.CH_2Cl$

B.P. 85-86° at 9 mm. (1)  $D_4^{20} = 1.2015$  (1)  $n_D^{20} = 1.43821$  (1)  
 60° at 1.3 mm. (1)

Colorless oil.

[For prepn. (80% yield (1)) from ethylene glycol monomethyl ether (1:6405) + chloroacetyl chloride (3:5235) in  $CHCl_3$  see (1).]

$\bar{C}$  on shaking with aq. saponifies to  $\beta$ -methoxyethanol (1:6405) + chloroacetic ac. (3:1370); titration of aq. soln. neutralizes 1 equiv. alk. (i.e., Sap. Eq. = 188.5).

3:9285 (1) Meerwein, Sönke, *J. prakt. Chem.* (2) **137**, 319-320 (1933).

- 3:9287 *ter*-AMYL HYPOCHLORITE  $C_5H_{11}OCl$  Beil. I —  
 (Dimethyl-ethyl-carbonyl hypochlorite)  $CH_2.CH_2-\overset{\overset{CH_3}{|}}{C}-CH_3$   
 $|$   
 $OCl$  I<sub>1</sub>—  
 I<sub>2</sub>-(423)

B.P. see text.  $D_4^{25} = 0.8547$  (1)

[See also *ter*-butyl hypochlorite (3:7165).]

Yellow mobile liquid with irritating odor and giving vapor which violently attacks eyes and mucous membranes (1). —  $\bar{C}$  boils with considerable decomposition; a thermometer in the vapor recorded 76° at 752 mm., but this cannot, of course, be regarded as a h.p. (1).

$\bar{C}$  is relatively stable and even after 2 months (in dark) is practically unchanged (1); for study of stability of  $\bar{C}$  in aq. or in  $CCl_4$  see (2). —  $\bar{C}$  on exposure to bright sunlight dec. quietly with evolution of heat leaving a colorless liq. contg. acetone (1:5400) and other prods.

[For prepn. of  $\bar{C}$  from *ter*-amyl alc. (1:6160) with  $Cl_2$  in aq. alk. (1) (3) or alk. earth (4) or with aq.  $HOCl$  in pres. of  $CCl_4$  (90% yield (5)) (2) see indic. refs.]

$\bar{C}$  with  $KI$  +  $AcOH$  liberates  $I_2$  quant. according to equation  $C_5H_{11}OCl + 2HI \rightarrow C_5H_{11}OH + HCl + I_2$  (use in quant. detn. of  $\bar{C}$  (1)).

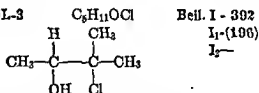
[For reactn. of  $\bar{C}$  with  $R_2C=NMgX$  cpds. to yield *N*-chloroimines see (3); for reactn. of  $\bar{C}$  with Schiff's bases see (5) (6).]



3:9287 (1) Chattaway, Backehurg, *J. Chem. Soc.* 123, 2999-3003 (1923). (2) Taylor, MacMullen, Gammat, *J. Am. Chem. Soc.* 47, 397-398 (1925). (3) Hauser, Humble, Haus, *J. Am. Chem.*

639-648 (1936); *Cent.* 1937, I 1674; *C.A.* 31, 3459 (1937).

3:9290 *d,l*-2-CHLORO-2-METHYLBUTANOL-3  
( $\alpha$ -Chloroisopropyl-methyl-carbinol)



No physical constants on  $\bar{C}$  appear to be recorded.

[For prepn. of  $\bar{C}$  from 2,3-epoxy-2-methylbutane (trimethylethylene oxide) [Beil. XVII-18] by addn. of HCl see (1).]

$\bar{C}$  passed over clay at 350° and 18 mm. pressure yields (2) 2-methylbutadiene-1,3 (isoprene) (1:8020).

3:9290 (1) Henry, *Compt. rend.* 144, 311 (1907); *Rec. trav. chim.* 26, 430-433 (1907). (2) Badische Anilin und Soda Fabrik, Ger. 255,519, Jan 3, 1913; *Cent.* 1913, I 476.

3:9295 5-CHLOROPENTANOL-1 CH<sub>2</sub>.(CH<sub>2</sub>)<sub>3</sub>.CH<sub>2</sub>OH C<sub>6</sub>H<sub>11</sub>OCl      Beil. S.N. 24  
( $\omega$ -Chloro-*n*-amyl alcohol)

B.P. 114° at 16 mm. (1)

[For prepn. of  $\bar{C}$  from  $\alpha,\omega$ -pentamethylene glycol (1:6519) with SOCl<sub>2</sub> (35% yield (2)) or with S<sub>2</sub>Cl<sub>2</sub> (35% yield (1)) see indic. refs.]

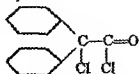
$\bar{C}$  with aliphatic mercaptans has apparently not been studied. [However, 5-chloro-*n*-amyl acetate (see below) with MeSH in MeOH/KOH yields (1) 5-hydroxy-*n*-amyl methyl sulfide, h.p. 121° at 16 mm.,  $D_4^{20} = 0.9846$ ,  $n_D^{20} = 1.488185$  (corresp. *N*-phenylcarbamate, m.p. 43.5°); this prod. with SOCl<sub>2</sub> gives (75% yield (3)) 5-chloro-*n*-amyl methyl sulfide, b.p. 94° at 15 mm.,  $D_4^{20} = 1.0300$ ,  $n_D^{20} = 1.48597$ . — Similarly 5-chloro-*n*-amyl acetate with EtSH in alc. KOH gives (68% yield (4)) 5-hydroxy-*n*-amyl ethyl sulfide, h.p. 135° at 20 mm.; this prod. with SOCl<sub>2</sub> + diethylaniline in CCl<sub>4</sub> gives (64% yield (4)) 5-chloro-*n*-amyl ethyl sulfide h.p. 122° at 25 mm. (4).]

$\bar{C}$  with aromatic mercaptans has apparently not been studied. [However, 5-chloro-*n*-amyl acetate (see below) with thiophenol in alc. KOH gives (1) 5-hydroxy-*n*-amyl sulfide, ndls. from lt. pet., m.p. 31.5° (corresp. *N*-phenylcarbamate, m.p. 59°); this prod. with SOCl<sub>2</sub> + dimethylaniline in CHCl<sub>3</sub> gives (3) 5-chloro-*n*-amyl phenyl sulfide, h.p. 174° at 14 mm., al. dec., 140° at 1 mm.,  $D_4^{20} = 1.1065$ ,  $n_D^{20} = 1.56040$ .]

$\bar{C}$  with Et<sub>2</sub>NH appears never to have been studied. [However, the prod. to be expected, viz., 5-(diethylamino)pentanol-1, h.p. 131° at 23-24 mm. (5), 125° at 18 mm. (6),  $D_4^{20} = 0.9842$  (5),  $n_D^{20} = 1.4642$  (5), has been reported by other means; this prod. with SOCl<sub>2</sub> in CHCl<sub>3</sub> would be expected to yield 5-(diethylamino)-*n*-amyl chloride, but this cannot be isolated in the free state owing to its isomerization (7) to *N*-ethyl-1-ethyl-2-methylpyrrolidinium chloride.]

$\bar{C}$  with morpholine gives (8) alm. quant. 5-(4-morpholinyl)pentanol-1, h.p. 133.0-133.5° at 5 mm.,  $D_4^{25} = 1.005$ ,  $n_D^{25} = 1.4755$  (corresp. *N*-phenylcarbamate, m.p. 55.5-57.0° cor.) (8). —  $\bar{C}$  (1 mole) with *N*-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (2) in alm. 100% yield (as salt) *N*-(5-hydroxy-*n*-amyl)-*N'*-phenylpiperazine, m.p. 74.0-75.0° cor. (corresp. *N*-phenylcarbamate, m.p. 100.0-101.5° cor.) (2).

3:0885  $\alpha$ -CHLORO-DIPHENYLACETYL CHLORIDE  $C_{14}H_{10}OCl_2$  Beil. IX - 675  
(Diphenyl-chloro-acetyl chloride) IX<sub>1</sub>-(283)



M.P. 51° (1) B.P. 180° at 14 mm. (3)  
50° (2) (8) (11) 179-180° at 14 mm. (8) (11)  
49-50° (3)  
48.5-49.5° (9)

Cryst. from ligr.

[For prepn. of  $\bar{C}$  from benzoic acid ( $\alpha$ -hydroxy-diphenyl-acetic acid) (1:0770) with 2 moles  $PCl_5$  at 120-130° (2), at 100° (8) (68% yield (9)), or with excess  $PCl_5$  in  $C_6H_6$  at room temp. (7) see indic. refs. (Note that benzoic acid dissolvd in undil.  $SOCl_2$  yields (4) benzophenone (1:5150), that benzoic acid treated with 3 moles  $SOCl_2$  in  $CCl_4$  for several days at room temp. ppts. (5) diphenylchloroacetic acid (3 3585), m.p. 118-119° dec., and that benzoic acid in  $CCl_4$  with 6 moles  $SOCl_2$  refluxed for several days yields (5) on concn. of the soln. diphenyl-chloro-acetic anhydride [Beil. IX<sub>1</sub>-(228)], m.p. 129° (5).] — For formn. of  $\bar{C}$  from diphenylketene [Beil. VII-471, VII<sub>1</sub>-(254)] with  $SOCl_2$  or  $SO_2Cl_2$  by htg. at 100° in s.t. in absence of air (1), or from diphenyldiazomethane [Beil. VII-418, VII<sub>1</sub>-(226)] with liq. phosgene in pet. ether in s.t. (92% yield), see (6) ]

[For abnormal reactn. of  $\bar{C}$  with  $C_6H_5MgBr$  see (9) (10); for reactn. of  $\bar{C}$  with Zn filings in dry ether yielding diphenylketene (above) see (11), for reactn. of  $\bar{C}$  with phenylhydroxylamine in ether giving quant. yield of anhydro-[*N*-phenyl-benzilhydroxamic acid] [Beil. XXVII<sub>1</sub>-(290)], cryst. from MeOH, m.p. 72-73°, see (12).]

$\bar{C}$  in ether treated with gaseous  $NH_3$  (2) (13) yields  $\alpha$ -chloro-diphenylacetamide, m.p. 115° (2), 111-113° (13). [This product on boilg. with aq. yields (2) benzilamide, m.p. 154° (2) ]

$\bar{C}$  dissolvd. in dry ether and treated with 2 moles aniline in dry ether ppts aniline hydrochloride and from the filtrate addn. of pet. ether ppts (3)  $\alpha$ -chloro-diphenyl-acet-anilide, m.p. 85° (3); this prod. on htg. with more aniline or  $\bar{C}$  warmed with 4 moles aniline yields (3)  $\alpha$ -anilido-diphenyl-acet-anilide, ndls. from alc., m.p. 181-182° (3) [Both the first prod. (on treatment with  $Na_2CO_3$ ) and the latter prod. (on HCl hydrolysis) yield (3) benzoic acid anilide, m.p. 175° (3).]

3:0883 (1) Staudinger, Göhring, Scholler, *Ber* 47, 47-48 (1914) (2) Bickel, *Ber* 22, 1538-1539 (1859). (3) Klinger, *Ann.* 359, 255-264 (1912). (4) Meyer, *Monatsh.* 22, 793 (1901). (5) Stoll, *Ber.* 43, 2471-2473 (1910). (6) Staudinger, Anthes, Pfenniger, *Ber* 49, 1939-1940 (1916). (7) Sedur, Nadkaring, *Proc. Indian Acad. Sci.* 12-A, 266-269 (1940), *C.A.* 35, 1398 (1941). (8) Staudinger, *Ann.* 356, 72-75 (1907). (9) McKenzie, Boyle, *J. Chem. Soc.* 119, 1137-1139 (1921). (10) Boyle, McKenzie, Mitchell, *Ber* 70, 2153-2160 (1937). (11) Staudinger, *Ber.* 38, 1735-1736 (1905). (12) Staudinger, Jelagin, *Ber* 44, 371-373 (1911). (13) Steinkopf, *Ber.* 41, 3593 (1908).

3:0900  $\beta$ -NAPHTHOYL CHLORIDE

$C_{11}H_7OCl$

Beil. IX - 657

IX<sub>1</sub>—



M.P. 51° (1) B.P. 304-306° (2)  
43° (2)

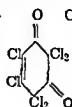
## CHAPTER XXI

### DIVISION C. LIQUIDS WITH BOILING POINTS REPORTED ONLY UNDER REDUCED PRESSURE

3:9300-3:9599 ( $C_6-C_8$  inclusive)

(Arranged in sequence of empirical formulas)

— 1,2,4,4,6,6-HEXACHLOROCYCLOHEXEN-  
1-DIONE-3,5  
("Hexachlororesorcinol")



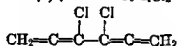
$C_6O_2Cl_6$  Beil. VII - 272  
VII<sub>1</sub>—

B.P. 159-160° at 13-15 mm.

M.P. 115°

See 3:3470. Division A: Solids.

3:9300 3,4-DICHLOROHEXATETRAENE-1,2,4,5  $C_6H_4Cl_2$  Beil. S.N. 14



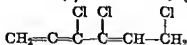
B.P. 38-40° at 8 mm. (1)

$D_4^{20} = 1.1819$  (1)  $n_D^{20} = 1.5456$  (1)

[For prepn. of  $\bar{C}$  from 1,3,4,6-tetrachlorohexadiene-2,4 (3:9306) with 15% excess KOH in abs. MeOH at 10-15° (a much larger amt. of 1,3,4-trichlorohexatriene-2,4,5 (3:9302) is also formed) see (1).]

3:9300 (1) Coffman, Carothers, *J. Am. Chem. Soc.* 55, 2040-2047 (1933).

3:9302 3,4,6-TRICHLOROHEXATRIENE-1,2,4  $C_6H_3Cl_3$  Beil. S.N. 13



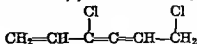
B.P. 50° at 1 mm. (1)

$D_4^{20} = 1.3132$  (1)  $n_D^{20} = 1.5517$  (1)

[For prepn. of  $\bar{C}$  from 1,3,4,6-tetrachlorohexadiene-2,4 (3:9306) with 15% excess KOH in abs. MeOH at 10-15° (a small amt. of 3,4-dichlorohexatetraene-1,2,4,5 (3:9300) is also formed) see (1).]

3:9302 (1) Coffman, Carothers, *J. Am. Chem. Soc.* 55, 2040-2047 (1933).

3:9304 3,6-DICHLOROHEXATRIENE-1,3,4  $C_6H_4Cl_2$  Beil. S.N. 13



B.P. 45-46° at 3 mm. (1)

$D_4^{20} = 1.1807$  (1)  $n_D^{20} = 1.5195$  (1)

38° at 1 mm. (1)

—— 5-Chloro-*n*-amyl acetate: b.p. 103° at 18 mm.,  $D_4^{20} \approx 1.0648$ ,  $n_D^{20} = 1.43791$  (1).

① 5-Chloro-*n*-amyl *N*-phenylcarbamate: m.p. 72° (1).

3:9295 (1) Bennett, Heathcoat, *J. Chem. Soc.* 1929, 273-274. (2) Anderson, Pollard, *J. Am. Chem. Soc.* 61, 3439-3440 (1939). (3) Bennett, Heathcoat, Mosses, *J. Chem. Soc.* 1929, 2569-2571. (4) Bennett, Turner, *J. Chem. Soc.* 1933, 814-815. (5) Magidson, Strukow, *Arch. Pharm.* 271, 575 (1933). (6) von Braun, *Ber.* 49, 974 (1916). (7) Ciemo, Hook, *J. Chem. Soc.* 1936, 608-609. (8) Anderson, Pollard, *J. Am. Chem. Soc.* 61, 3440-3441 (1939).

[For prepn. of  $\bar{C}$  from 3,6-dichlorohexatriene-1,3,4 (3:9304) with conc. HCl contg.  $Cu_2Cl_2$  by shaking for 12 hrs. at 27° see (1).]

$\bar{C}$  refluxed with stirring for 7 hrs. with aq.  $Na_2CO_3$  gives (1) chloride ion corresp. to three halogen atoms but the org. product was not identified.

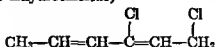
$\bar{C}$  on oxidn. with alk.  $KMnO_4$  for 4 hrs. at 30–40° yields (1) chloroacetic acid (3:1370).

3:9308 (1) Coffman, Carothers, *J. Am. Chem. Soc.* 55, 2040–2047 (1933).

3:9310 1,3-DICHLOROHEXADIENE-2,4  
(Divinylacetylene dihydrochloride)

$C_6H_8Cl_2$

Beil. S.N. 12



B.P. 80–82° at 17 mm. (1)

$D_4^{20} = 1.1456$  (1)  $n_D^{20} = 1.5271$  (1)

[For prepn. of  $\bar{C}$  (53% yield (1)) from divinylacetylene by shaking with 12 N HCl contg.  $Cu_2Cl_2$  see (1).]

$\bar{C}$  refluxed with NaOAc + AcOH yields (by reactn. of one chlorine atom) 1-acetoxy-3-chlorohexadiene-2,4, b.p. 84–85° at 3 mm.,  $D_4^{20} = 1.0915$ ,  $n_D^{20} = 1.4890$  (1). — Similarly  $\bar{C}$  on htg. with MeOH/KOH yields (1) 1-methoxy-3-chlorohexadiene-2,4, n.p. 88–92° at 30 mm.,  $D_4^{20} = 1.0239$ ,  $n_D^{20} = 1.4928$  (1).

$\bar{C}$  on oxidn. with aq.  $KMnO_4$  in  $K_2CO_3$  soln. gives (1) chloroacetic acid (3:1370) + acetic acid (1:1010).

$\bar{C}$  with naphthoquinone-1,4 (1:9040) or with maleic anhydride (1:0625) gives (1) only a small amt. of dark gummy material.

3:9310 (1) Coffman, Nieuwland, Carothers, *J. Am. Chem. Soc.* 55, 2048–2051 (1933).

3:9312 3-CHLOROHEXADIENE-1,3

Cl

$C_6H_7Cl$

Beil. S.N. 12



B.P. 68.2–69° at 117 mm. (1)

$D_4^{20} = 0.9390$  (1)  $n_D^{20} = 1.4770$  (1)

[For prepn. of  $\bar{C}$  from  $\alpha$ -ethyl- $\beta$ -vinylacetylene by shaking with conc. HCl contg.  $Cu_2Cl_2$  +  $NH_4Cl$  see (1).]

[For polymerization of  $\bar{C}$  see (1) (2).]

$\bar{C}$  on htg. with 2 pts. naphthoquinone-1,4 (1:9040) for 2 hrs. at 100° then suspended in alc. NaOH and aerated gives (1) 2-chloro-1-ethylanthraquinone, yel. ndls. from alc., m.p. 151–152° (1).

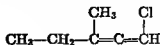
[For study of another chlorohexadiene obtd. from allyl chloride (3:7035) by actn. of  $NaNH_2$  in liq.  $NH_3$  see (3) ]

3:9312 (1) Jacobson, Carothers, *J. Am. Chem. Soc.* 55, 1624–1627 (1933). (2) Carothers, Coffman (to du Pont), U.S. 1,950,441, March 13, 1934; *Cent.* 1934, II 1037; *C.A.* 28, 3270 (1934). (3) Kharasch, Nudenberg, Sternfeld, *J. Am. Chem. Soc.* 62, 2034–2035 (1940).

3:9314 1-CHLORO-3-METHYLPENTADIENE-1,2

$C_6H_9Cl$

Beil. S.N. 12



B.P. 68–70° at 100 mm. (1)

$D_4^{20} = 0.9562$  (1)  $n_D^{20} = 1.46967$  (1)

[For formn. of  $\bar{C}$  from 3-methylpentyn-1-ol-3 (ethyl-ethynyl-methyl-carbinol) by shaking

[For prepn. of  $\bar{C}$  from hexadien-2,5-yne-3 (divinylacetylene) (2) with  $Cl_2$  in  $CCl_4$  at  $-50^\circ$  (20-25% yield together with other products) or in small yield with  $HOCl$  see (1).]

$\bar{C}$  slowly polymerizes, changing in 3 months to a viscous sirup (1).

$\bar{C}$  on cat. hydrogenation in  $EtOAc$  yields *n*-hexane (1:8530), b.p.  $69-70^\circ$  (1).

$\bar{C}$  on cat. hydrogenation in  $CCl_4$  at  $0^\circ$  gives (1) 1,3,4,6-tetrachlorohexadiene-2,4  
 $n_D^{20} = 1.5458$  (1).

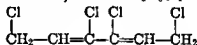
12 hrs. at  $27^\circ$  adds  $HCl$  yielding (1) 3,3,6-trichlorohexadiene-1,4 (3:9308) q.v.

$\bar{C}$  refluxed with stirring for 8 hrs. with 6 pts. aq. contg. 2 moles  $Na_2CO_3$  gives (1) chloride ion corresp. to one of the two initial halogenations together with a soft sticky resin. —  $\bar{C}$  with  $MeOH/KOH$  at  $10-15^\circ$  or with  $NaOMe$  in dry  $MeOH$  loses 1  $HCl$  giving excellent yield (1) of 3-chlorohexatetraene-1,3,4,5 (3:7735).

$\bar{C}$  on oxidn. with aq.  $KMnO_4$  yields (1) chloroacetic acid (3:1370).

3:9304 (1) Coffman, Carothers, *J. Am. Chem. Soc.* 55, 2040-2047 (1933). (2) Nieuwland, Calcott, Downing, Carter, *J. Am. Chem. Soc.* 53, 4200-4202 (1931).

3:9306 1,3,4,6-TETRACHLOROHEXADIENE-2,4  $C_6H_2Cl_4$  Beil. S.N. 12



B.P.  $84-89^\circ$  at 2 mm. (1)

$D_4^{20} = 1.4013$  (1)  $n_D^{20} = 1.5465$  (1)

[For prepn. of  $\bar{C}$  from hexadien-2,5-yne-3 (divinylacetylene) (2) with  $Cl_2$  at  $-40^\circ$  to  $-50^\circ$  (together with other products) see (1).]

$\bar{C}$  treated directly with  $Cl_2$  for 8 hrs. at  $60-70^\circ$  gives (23% yield (1)) 1,2,3,4,5,6-hexachlorohexene-3 (3:1220), m.p.  $57-58^\circ$  (1)

$\bar{C}$  refluxed for 8 hrs. with stirring with aq.  $Na_2CO_3$  soln. gives (1) chloride ion corresp. to two of the initial four chlorine atoms. —  $\bar{C}$  with abs.  $MeOH/KOH$  at  $10-15^\circ$  loses  $HCl$  in each of two ways yielding (1) both 1,3,4-trichlorohexatriene-2,4,5 (3:9302) and 3,4-dichlorohexatetraene-1,2,4,5 (3:9300).

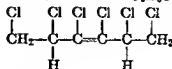
$\bar{C}$  on oxidn. with aq.  $KMnO_4$  for 5 hrs. at  $35-40^\circ$  gives (1) chloroacetic acid (3:1370).

3:9306 (1) Coffman, Carothers, *J. Am. Chem. Soc.* 55, 2040-2047 (1933). (2) Nieuwland, Calcott, Downing, Carter, *J. Am. Chem. Soc.* 53, 4200-4202 (1931)

1,2,3,4,5,6-HEXACHLOROHEXENE-3

$C_6H_2Cl_6$

Beil. S.N. 11



B.P.  $110-112^\circ$  at 2 mm.

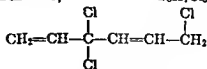
M.P.  $58-59^\circ$

See 3:1220. Division A: Solids.

3:0308 3,3,6-TRICHLOROHEXADIENE-1,4

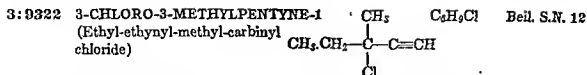
$C_6H_3Cl_3$

Beil. S.N. 12



B.P.  $100-103^\circ$  at 4 mm. (1)

$D_4^{20} = 1.3030$  (1)  $n_D^{20} = 1.5585$  (1)

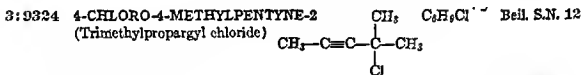


B.P. 55° at 130 mm. (1)  $D_4^{20} = 0.9163$  (1)  $n_D^{20} = 1.4330$  (1) (2)  
 51-52° at 135 mm. (2) 0.9140 (2)  
 48-50° at 100 mm. (3) 0.9141 (3)  $n_D^{20} = 1.42963$  (3)

[For prepn. of  $\bar{\text{C}}$  from 3-methylpentyn-1-ol-3 (ethyl-ethynyl-methyl-carbinol) by shaking with conc. HCl (40% yield (2)) best overnight (60% yield (1)); if the acid also contains  $\text{Cu}_2\text{Cl}_2 + \text{NH}_4\text{Cl}$ ,  $\bar{\text{C}}$  is accompanied (3) by 1-chloro-3-methylpentadiene-1,2 (3:9314).] [Note that dry HCl at 0° reacts with the alc. only slightly while  $\text{PCl}_3$  + pyridine gave a product difficult to purify (1).]

$\bar{\text{C}}$  with  $\text{CH}_3\text{MgBr}$  gives (66% yield (1)) 3,3-dimethylpentyne-1, b.p. 69° at 100 mm,  $D_4^{20} = 0.7610$ ,  $n_D^{20} = 1.4360$ ;  $\bar{\text{C}}$  with  $\text{C}_2\text{H}_5\text{MgBr}$  gives (61% yield (1)) 3-ethyl-3-methylpentyne-1, b.p. 88° at 100 mm,  $D_4^{20} = 0.7714$ ,  $n_D^{20} = 1.4386$ . [In orig. paper these products are incorrectly numbered and named.]

*Chem. Soc.* 62, 1793-1800 (1940). (2) K. N. Campbell, B. K. 0, 2882-2884 (1938). (3) Favorskaya, Zakharova, *J. Gen. C.A.* 34, 7844 (1940).

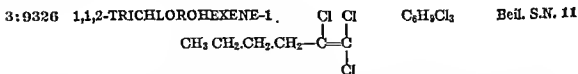


B.P. 57-61° at 47 mm. (1)  $n_D^{20} = 1.4143$  (1)

[For prepn. of  $\bar{\text{C}}$  (33% yield (1)) from 2-methylpropyn-3-ol-2 (trimethylpropargyl alcohol) with  $\text{PCl}_3$  in dry ether see (1).]

$\bar{\text{C}}$  in acetone refluxed 4 hrs. with  $\text{K}_2\text{CO}_3$  and phenol gives (69% yield (1)) phenyl trimethylpropargyl ether,  $n_D^{20} = 1.3408$ , but undistillable without decomposition (1).

3:9324 (1) Hurd, Cohen, *J. Am. Chem. Soc.* 53, 1074 (1931).



B.P. 90-93° at 10 mm. (1) (2)  $D_4^{25} = 1.225$  (1) (2)  $n_D^{25} = 1.4760$  (1) (2)

This compound was at first (2) thought to be 1,2,2-trichlorohexane but later (1) was established as  $\bar{\text{C}}$ .

[For formn. of  $\bar{\text{C}}$  from hexyne-1 (*n*-butylacetylene) (1:8055) with  $\text{Cl}_2$  in aq. *ter*-BuOH, MeOAc, AcOH, or  $\text{Ac}_2\text{O}$  at 45° (2) or in 35% aq. HCl, 30% aq.  $\text{H}_2\text{SO}_4$ , 30%  $\text{H}_3\text{PO}_4$ , or 22% MeOH/HCl (1) see indic. refs.]

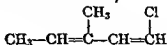
3:9326 (1) Norris, Hennion, *J. Am. Chem. Soc.* 62, 449-450 (1940). (2) Norris, Vogt, Hennion, *J. Am. Chem. Soc.* 61, 1460-1461 (1939).

with conc. HCl contg.  $\text{Cu}_2\text{Cl}_2 + \text{NH}_4\text{Cl}$  see (1) (considerable 3-chloro-3-methylpentyne-1 (3:9322) is also formed.)

$\bar{\text{C}}$  on stdg. 8 months with  $\text{Cu}_2\text{Cl}_2$ ,  $\text{NH}_4\text{Cl}$ , plus a few drops conc. HCl isomerized to 1-chloro-3-methylbutadiene-1,3 (3:7355) (1).

3:9314 (1) Favorskaya, Zakharova, *J. Gen. Chem. (U.S.S.R.)* 10, 446-450 (1940); *C.A.* 34, 7844 (1940).

3:9316 1-CHLORO-3-METHYLPENTADIENE-1,3  $\text{C}_6\text{H}_9\text{Cl}$  Beil. S.N. 12



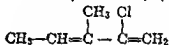
B.P. 62-63° at 100 mm. (1)  $D_4^{20} = 0.9574$  (1)  $n_D^{20} = 1.47714$  (1)

[For prepn. of  $\bar{\text{C}}$  from 1-chloro-3-methylpentadiene-1,2 (3:9314) by stdg 8 months with  $\text{Cu}_2\text{Cl}_2$ ,  $\text{NH}_4\text{Cl}$ , plus a few drops conc. HCl see (1) ]

$\bar{\text{C}}$  reacts with maleic anhydride (1-0625) to give a mixt. from which after hydrolysis two acids, one m.p. 218-220°, the other, m.p. 350-351°, are obtd. (1).

3:9316 (1) Favorskaya, Zakharova, *J. Gen. Chem. (U.S.S.R.)*, 10, 446-450 (1940); *C.A.* 34, 7844 (1940).

3:9318 2-CHLORO-3-METHYLPENTADIENE-1,3  $\text{C}_6\text{H}_9\text{Cl}$  Beil. S.N. 12



B.P. 57-60° at 96 mm. (1)  $D_4^{20} = 0.9437$  (1)  $n_D^{20} = 1.4671$  (1)

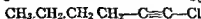
[For prepn. of  $\bar{\text{C}}$  from 3-methylpenten-2-yne-4 in 22% yield (1) by shaking for 5½ hrs at 20° with conc. HCl contg.  $\text{Cu}_2\text{Cl}_2 + \text{NH}_4\text{Cl}$  see (1).]

$\bar{\text{C}}$  on htg with 2 pts. naphthoquinone-1,4 (1.9040) for 1 hr. at 100° gives (1) on cooling 2-chloro-3,4-dimethyltetrahydroanthraquinone, colorless ndls from aq. acetone, m.p. 107° (1); suspension of this intermediate in dil. alc. NaOH and aeration until the purple solution becomes yellow gives (1) 2-chloro-3,4-dimethylanthraquinone, yel. cryst. from AcOH, m.p. 171.5° (1).

[For polymerization of  $\bar{\text{C}}$  see (1) (2) ]

3:9318 (1) Carothers, Coffman, *J. Am. Chem. Soc.* 54, 4075-4076 (1932). (2) Carothers, Coffman (to du Pont), U.S. 1,950,441, March 13, 1934; *Cent.* 1934, II 1038, *C.A.* 28, 3270 (1934).

3:9320 1-CHLOROHEXYNE-1  $\text{C}_6\text{H}_9\text{Cl}$  Beil. S.N. 12



B.P. 47° at 55 mm. (1)  $n_D^{25} = 1.43350$  (1)

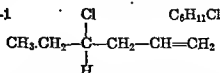
[For prepn. of  $\bar{\text{C}}$  from hexyne-1 (1:8055) by conversion in liq.  $\text{NH}_3$  to  $\text{C}_4\text{H}_9\text{C}\equiv\text{C}-\text{K}$  and treatment of this prod. in ether suspension with  $\text{Cl}_2$  at -32° see (2) (3); for prepn. of  $\bar{\text{C}}$  from  $\text{C}_4\text{H}_9\text{C}\equiv\text{C}.\text{Na}$  with benzenesulfonyl chloride in ether see (1) (4).]

$\bar{\text{C}}$  in MeOH + HgO +  $\text{BF}_3$  as specified (2) adds 2 MeOH giving in 83% yield 1-chloro-2,2-dimethoxyhexane, b.p. 77-80° at 14 mm,  $D_4^{25} = 0.9873$ ,  $n_D^{25} = 1.4305$  (2).

3:9320 (1) Pfau, Wenzke, *J. Am. Chem. Soc.* 56, 1106-1107 (1934). (2) Verbanc, Hennon, *J. Am. Chem. Soc.* 60, 1711-1713 (1938). (3) McCusker, Vogt, *J. Am. Chem. Soc.* 59, 1303-1309 (1937). (4) Truchet, *Ann. chim.* (10) 16, 309-416 (1931).



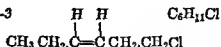
3:9332 (1) Hennion, Welsh, *J. Am. Chem. Soc.* **62**, 1367-1368 (1940). (2) Norris, Vogt, Hennion, *J. Am. Chem. Soc.* **61**, 1460-1461 (1939). (3) Norris, Hennion, *J. Am. Chem. Soc.* **62**, 449-450 (1940).

3:9334 *d,l*-3-CHLOROHEXENE-1 $\text{C}_6\text{H}_{11}\text{Cl}$ 

Beil. S.N. 11

[This compound is as yet unrecorded: a dextrorotatory isomeride has been prepared (1) from levorotatory hexen-1-ol-3 with  $\text{PCl}_3$  in pyridine. Although distd. at 20 mm., no b.p. was reported (1).]

3:9334 (1) Levene, Haller, *J. Biol. Chem.* **83**, 595 (1929).

3:9336 *cis*-1-CHLOROHEXENE-3 $\text{C}_6\text{H}_{11}\text{Cl}$ 

Beil. S.N. 11

B.P. 59-61° at 60 mm. (1)

 $D_4^{24} = 0.900$  (1)  $n_D^{24} = 1.435$  (1)

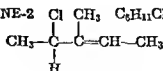
Two geometrical stereoisomers of this structure are theoretically possible, but only that with the *cis* configuration ( $\bar{C}$ ) has as yet been recognized.

[For prepn. of  $\bar{C}$  from *cis*-hexen-3-ol-1 [Beil. I<sub>1</sub>-(229), I<sub>2</sub>-(486)] (1) (2) (b.p. 156.1° at 760 mm. (3), 63.3° at 14 mm. (3),  $D_4^{21.6} = 0.8478$  (2),  $n_D^{24} = 1.4373$  (2), 3,5-dinitrobenzoate, m.p. 44.5-46°, *N*-( $\alpha$ -naphthyl)carbamate, m.p. 80° (4)) with  $\text{SOCl}_2$  + pyridine in  $\text{CHCl}_3$  (72% yield (1)) see (1).]

$\bar{C}$  with NaI htd. 12 hrs. in acetone yields (1) 1-iodohexene-3, b.p. 62-63° at 12 mm.,  $D_4^{21} = 1.469$  (1).

$\bar{C}$  fails to react with activated Mg in dry ether, but the corresponding iodo cpd. (see above) yields the corresp. RMgI (1), and a mixt. of both can be used (5).

3:9336 (1) Ruzicka, Schinz, *Helv. Chim. Acta* **17**, 1606 (1934). (2) Stoll, Rouvé, *Helv. Chim. Acta* **21**, 1542-1547 (1938). (3) von Rechenberg, *J. prakt. Chem.* (2) **101**, 120 (1920). (4) van Romburgh, *Proc. Acad. Sci. Amsterdam* **22**, 758-761 (1920); *C.A.* **14**, 2780 (1920). (5) Stoll, Bolle, *Helv. Chim. Acta* **21**, 1551 (1938).

3:9338 *d,l*-4-CHLORO-3-METHYLPENTENE-2  
( $\alpha,\beta,\gamma$ -Trimethylallyl chloride) $\text{C}_6\text{H}_{11}\text{Cl}$ 

Beil. I—

I<sub>1</sub>-(90)I<sub>2</sub>—

B.P. 41-43° at 31 mm. (1)

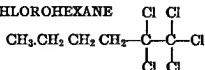
Note: although the product is as yet unrecognized,  $\bar{C}$  by virtue of allylic transposition may conceivably be in equilibrium with its synionic isomer 2-chloro-3-methylbutene-3.

[For prepn. of  $\bar{C}$  (75-80% yield (1)) from 3-methylpenten-2-ol-4 [Beil. I-445] by distn. with 6 *N* HCl see (1).]

$\bar{C}$  with quinoline at 170° loses HCl giving (66% yield (1)) 3-methylpentadiene-1,3 [Beil. I<sub>1</sub>-(118), I<sub>2</sub>-(231)], b.p. 76°.

3:9338 (1) Abelmann, *Ber.* **43**, 1570, 1583 (1910).

3:9328 1,1,1,2,2-PENTACHLOROHEXANE  $\text{C}_6\text{H}_9\text{Cl}_5$  Beil. S.N. 10



B.P. 129-131° at 10 mm. (1)

$D_4^{25} = 1.370$  (1)  $n_D^{25} = 1.4980$  (1)

[For formn. of  $\bar{\text{C}}$  from hexyne-1 (*n*-butylacetylene) (1:8055) with  $\text{Cl}_2$  in  $\text{MeOAc}$  at 45° (1) or in 35% aq.  $\text{HCl}$ , 30% aq.  $\text{H}_2\text{SO}_4$ , 30% aq.  $\text{H}_3\text{PO}_4$ , or 22%  $\text{MeOH/HCl}$  (2) (together with other products) see indic. refs.]

3:9328 (1) Norris, Vogt, Hennion, *J. Am. Chem. Soc.* **61**, 1460-1461 (1939). (2) Norris, Hennion, *J. Am. Chem. Soc.* **62**, 449-450 (1940).

3:9330 1,2-DICHLOROHEXENE-1  $\text{C}_6\text{H}_{10}\text{Cl}_2$  Beil. S.N. 11



*cis* form

B.P. 88° at 30 mm. (1)

80-82° at 25 mm. (2)

$D_4^{25} = 1.0812$  (1)  $n_D^{25} = 1.4631$  (1)

$D_4^{25} = 1.076$  (2) 1.4629 (2)

*trans* form

B.P. 63-65° at 32 mm. (1)

55-57° at 25 mm. (2)

$D_4^{25} = 1.1167$  (1)  $n_D^{25} = 1.4576$  (1)

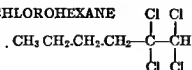
$D_4^{25} = 1.051$  (2) 1.4543 (2)

[For prepn. of  $\bar{\text{C}}$  (*cis* form) from 2-chlorohexene-1 (3:7530) with  $\text{Cl}_2$  in  $\text{CCl}_4$  at 35-40° (1) (yield 26.7% together with 25.4% of 1,1,2,2-tetrachlorohexane (3:9332)) (1) or in  $\text{Ac}_2\text{O}$ , or  $\text{AcOH}$  (2), see indic. refs.; for prepn. of  $\bar{\text{C}}$  (*trans* form) from hexyne-1 (1:8055) with  $\text{Cl}_2$  in  $\text{CCl}_4$  or heptane in pres. of trace of  $\text{SbCl}_5$  (yield 19.6% together with 30.6% yield of 1,1,2,2-tetrachlorohexane (3:9332)) (1) or in aq. or *ter*- $\text{BuOH}$  (2) see indic. refs.; for prepn. of  $\bar{\text{C}}$  (both forms) from hexyne-1 (1:8055) +  $\text{Cl}_2$  in conc.  $\text{HCl}$ , 30%  $\text{H}_2\text{SO}_4$ , 30%  $\text{H}_3\text{PO}_4$ , or  $\text{MeOH}$  satd. with  $\text{HCl}$  (together with other prods.) see (3) (4) or in  $\text{MeOAc}$  see (2).]

Neither *cis* nor *trans* forms of  $\bar{\text{C}}$  will add  $\text{HCl}$  even in pres. of  $\text{BiCl}_3$  (1) (3).

3:9330 (1) Hennion, Welsh, *J. Am. Chem. Soc.* **62**, 1367-1368 (1940). (2) Norris, Vogt, Hennion, *J. Am. Chem. Soc.* **61**, 1460-1461 (1939) (3) Norris, Hennion, *J. Am. Chem. Soc.* **62**, 449-450 (1940) (4) Verbanc, Hennion, *J. Am. Chem. Soc.* **60**, 1711-1713 (1938).

3:9332 1,1,2,2-TETRACHLOROHEXANE  $\text{C}_6\text{H}_8\text{Cl}_4$  Beil. S.N. 10



B.P. 99-101° at 14 mm. (1)

108-110° at 10 mm. (1)

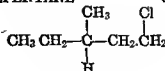
$D_4^{25} = 1.3096$  (1)  $n_D^{25} = 1.4888$  (1)

$D_4^{25} = 1.320$  (2) 1.4890 (2)

[For formn. of  $\bar{\text{C}}$  from hexyne-1 (*n*-butylacetylene) (1:8055) with  $\text{Cl}_2$  in aq.,  $\text{MeOAc}$ ,  $\text{Ac}_2\text{O}$ , or  $\text{AcOH}$  at 45° (1), or in 35% aq.  $\text{HCl}$ , 30% aq.  $\text{H}_2\text{SO}_4$ , 30% aq.  $\text{H}_3\text{PO}_4$ , or 22%  $\text{MeOH/HCl}$  (3), or in  $\text{CCl}_4$  +  $\text{SbCl}_5$  (30.6% yield (1)) (together with other products) see indic. refs.; for formn. of  $\bar{\text{C}}$  from 2-chlorohexene-1 (3:7530) with  $\text{Cl}_2$  in  $\text{C}_6\text{H}_6$  +  $\text{BiCl}_3$  at 35-40° (25.4% yield  $\bar{\text{C}}$  + 26.7% yield *cis* 1,2-dichlorohexene-1 (3:9330)) see (1).]

3:9348 *d,l*-1-CHLORO-3-METHYLPENTANE $C_6H_{13}Cl$ 

Beil. S.N. 10



$\bar{C}$  itself seems to be unreported.

[The dextrorotatory isomer of  $\bar{C}$  has, however, been studied (1) (2) (3). For prepn. of it from dextrorotatory 3-methylpentanol-1 with  $\text{SOCl}_2$  see (1); b.p.  $73^\circ$  at 100 mm. (1),  $D_4^{27} = 0.892$ ,  $n_D^{25} = 1.4210$  (1). — With Mg in dry ether this isomer yields (2) (3)  $\text{RMgCl}$  which with  $\text{CO}_2$  gives (2) (3) dextrorotatory 3-methylhexanoic acid-6, b.p.  $115^\circ$  at 16 mm. (2) (3),  $D_4^{22} = 0.923$  (3).]

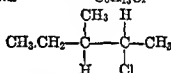
3:9348 (1) Levene, Marker, *J. Biol. Chem.* 91, 86 (1931). (2) Levene, Marker, *J. Biol. Chem.* 95, 11 (1932). (3) Levene, Marker, *J. Biol. Chem.* 95, 161 (1932).

3:9350 *d,l*-2-CHLORO-3-METHYLPENTANE

(sec.-Butyl-methyl-carbinyl chloride)

 $C_6H_{13}Cl$ 

Beil. S.N. 10



B.P.  $71.1-73.3^\circ$  at 160 mm. (1)

[For formn. of  $\bar{C}$  (together with other products) in reaction of 2-ethylhexanol-1 (1:6223) with  $\text{HCl} + \text{ZnCl}_2$  see (1)].

$\bar{C}$  with Mg + dry ether yields (1)  $\text{RMgCl}$  which with  $\text{O}_2$  yields (1) 3-methylpentanol-2 (1:6202); this alc. upon oxidn. with  $\text{CrO}_3/\text{H}_2\text{SO}_4$  yields (1) 3-methylpentanone-2 (2,4-dinitrophenylhydrazone, m.p.  $71.2^\circ$  (2),  $70.5-72.5^\circ$  (1)).

3:9350 (1) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938). (2) Drake, Veitch, *J. Am. Chem. Soc.* 57, 2624 (1935).

## 3-CHLOROCATECHOL

 $C_6H_5O_2Cl$ 

Beil. VI —

VI<sub>1</sub>-(388)VI<sub>2</sub>—

B.P.  $110-111^\circ$  at 11 mm.

M.P.  $47^\circ$

See 3:0745. Division A: Solids.

## 4-CHLOROCATECHOL

 $C_6H_5O_2Cl$ 

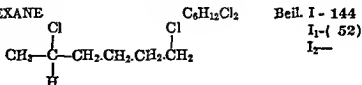
Beil. VI - 783

VI<sub>1</sub>-(389)VI<sub>2</sub>-(787)

B.P.  $139^\circ$  at 10 mm.

M.P.  $90-91^\circ$

See 3:2470. Division A: Solids.

3:9340 *d,l*-1,5-DICHLOROHEXANE

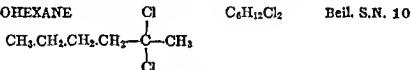
B.P. 74-78° at 10 mm. (1)

Heavy oil with agreeable odor. — Insol. aq.

[For prepn. of  $\bar{\text{C}}$  (50% yield (1)) from *N*-benzoyl-2-methylpiperidine (*N*-benzoyl- $\alpha$ -pipercoline) [Beil. XX-97] with  $\text{PCl}_3$  (1), from hexanediol-1,5 [Beil. I-484] or the corresponding internal ether, 2-methyltetrahydropyran [Beil. XVII-13], by repeated treatment with  $\text{HCl}$  (2), or from hexamethylenediamine [Beil. IV-269] with  $\text{NOCl}$  (3) see indic. refs.]

3:9340 (1) von Braun, Sobecki, *Ber.* 44, 1042-1043 (1911). (2) Lipp, *Ber.* 18, 3283-3286 (1885). (3) Ssolonma, *J. Russ. Phys.-Chem. Soc.* 30, 606-632 (1898); *Cent.* 1899, I 25.

## 3:9342 2,2-DICHLOROHEXANE



B.P. 68° at 49 mm. (1)

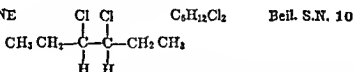
 $D_4^{25} = 1.0150$  (1)  $n_D^{25} = 1.4353$  (1)

[For formn. of  $\bar{\text{C}}$  (40% yield (1) together with 20% yield (1) of 2-chlorohexene-1 (3:7530)) from hexyne-1 (1:8055) with  $\text{HCl}$  gas +  $\text{BiCl}_3$  see (1)]

$\bar{\text{C}}$  htd. at 95° with soln. of solid  $\text{KOH}$  in *n*-propyl alc. gives (60.5% yield (1)) 2-chlorohexene-1 (3:7530).

3:9342 (1) Hennion, Welsh, *J. Am. Chem. Soc.* 62, 1367-1368 (1940).

## 3:9344 3,4-DICHLOROHEXANE

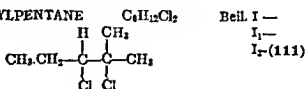


B.P. 69-70° at 30 mm. (1)

 $D_4^{20} = 1.055$  (1)  $n_D^{20} = 1.4490$  (1)

Colorless liq. with sweetish odor.

[For prepn. of  $\bar{\text{C}}$  from hexene-3 (1:8270) with  $\text{Cl}_2$  in  $\text{CHCl}_3$  at -30° to -40° (67% yield (1)), or with  $\text{SO}_2\text{Cl}_2$  at 40-50° (1), or with  $\text{PCl}_3$  in  $\text{CCl}_4$  (1) see (1).]

3:9344 (1) Spiegler, Tinker, *J. Am. Chem. Soc.* 61, 941-942 (1939).3:9346 *d,l*-2,3-DICHLORO-2-METHYLPENTANE

B.P. 82-84° at 42 mm. (1)

[For formn. of  $\bar{\text{C}}$  from 2-methylpentene-2 (1:8275) with  $\text{Cl}_2$  in  $\text{CHCl}_3$  (some 2-(or 3)-chloro-2-methylpentane (3:7490) is also formed) see (1)]

3:9346 (1) van Risseghem, *Bull. soc. chim. Belg.* 32, 149-150 (1923).

Cryst. pdr. from  $C_6H_6$  + lt. pet. (1). — Sol. ether,  $CHCl_3$ ,  $C_6H_6$ ; insol. aq.

[For prepn. of  $\bar{C}$  from  $\beta$ -naphthoic acid (1:0800) with  $PCl_5$  (2) (3) or with  $SOCl_2$  (100% yield (4)) (1) (5) see indic. refs.]

$\bar{C}$  with *ter* bases +  $K_2S_2O_8$  (6) or  $\bar{C}$  with calcium  $\beta$ -naphthoate at 150–160° (7) yields  $\beta$ -naphthoic acid anhydride, m.p. 134° (7) [cf.  $\alpha$ -naphthoyl chloride (3:6930)].

$\bar{C}$  corresp.  $\beta$ -naphthyl ketones: e.g., with biphenyl (3:10), 2,6- (11), and 2,7- (12) dimethylnaphthalene (13) with  $RMgX$  cpds. also yields  $\beta$ -naphthyl ketones; e.g., see (14).]

[For use of  $\bar{C}$  in prepn. of vat dyes from mono- and diamino-anthraquinones see (15).]

$\bar{C}$  with hydrazine hydrate yields (5) both  $\beta$ -naphthoylhydrazine ( $\beta$ -naphthoylhydrazide), cryst. from alc., m.p. 147.5° (5), and *N,N'*-bis-( $\beta$ -naphthoyl)hydrazine, cryst. from AcOH, m.p. 241° (5).

$\bar{C}$  on hydrolysis yields  $\beta$ -naphthoic acid (1:0800), m.p. 184°. — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see  $\beta$ -naphthoic acid (1:0800); in addition see below.

①  $\beta$ -Naphthoic  $\beta$ -naphthalide; ndls. from hot  $CHCl_3$ , m.p. 238° (4). [From  $\bar{C}$  +  $\beta$ -naphthylamine in  $C_6H_6$  (4).]

3:0900 (1) Bell, *J. Chem. Soc.* 1930, 1985. (2) Vieth, *Ann.* 180, 317–319 (1875). (3) Raiford, *Praktika* 56, 352 (1876). (4) Clar, *Ber.* 62, 1831 (1929). (5) Fieser, *Seligman, J. Am. Chem. Soc.* 59, 478–480 (1930). (6) Meyer, *Hopff* (to I.G.), *Ger.* 432,570, Aug. 7, 1926; *Cent.* 1926, II 2231.

(8) de Ceuster, *Cent.* 1932, II 1296. (9) Clar, *Ber.* 62, 1831 (1929). (10) Cook, *J. Chem. Soc.* 1931, 492. (11) Migita, *Bull. Chem. Soc. Japan* 7, 379 (1932). (12) Cook, *J. Chem. Soc.* 1931, 492. (13) Migita, *Bull. Chem. Soc. Japan* 7, 379 (1932). (14) Fieser, *Seligman, J. Am. Chem. Soc.* 59, 478–480 (1930). (15) Meyer, *Hopff* (to I.G.), *Ger.* 432,570, Aug. 7, 1926; *Cent.* 1926, II 2231.

### 3:0915 1,2,3,5-TETRACHLOROBENZENE



$C_6H_2Cl_4$

Beil. V - 204

V<sub>1</sub>-(113)

V<sub>2</sub>-(157)

M.P. 51° (1) (2) (3) B.P. 246° cor. (5)

50.5–51.6° (4)

50.3–51.3° (6)

50–51° (5) (7)

49° (8)

Ndls. from alc. — Spar. sol. cold alc.; eas. sol.  $C_6H_6$ , very eas. sol.  $CS_2$  or lgr. — Volatile with steam.

[For prepn. of  $\bar{C}$  from 2,4,6-trichloroaniline (Beil. XII-627, XII<sub>1</sub>-(312)] via diazotization (3:0900) with  $AlCl_3$  +  $S_2Cl_2$  in  $SO_2Cl_2$  at 40° (10% pure  $\bar{C}$  + 67% 1,2,4,5-tetrachlorobenzene (3:4115)) see (1); from (3:1672) with  $PCl_5$  +  $PCl_5$  in s.t. at 200–300° see Beil. V-204; fr

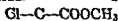
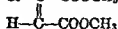
via tetrazotization and warming with  $Cu_2Cl_2$  see (7); for formn. of  $\bar{C}$  from (3:0900)

(3:0980) with  $AlCl_3$  +  $S_2Cl_2$  in  $SO_2Cl_2$  at 40° (10% pure  $\bar{C}$  + 67% 1,2,4,5-tetrachlorobenzene (3:4115)) see (1); from (3:1672) with  $PCl_5$  +  $PCl_5$  in s.t. at 200–300° see Beil. V-204; fr (10) or (sulfonyle chloride) (4) on hgt. in s.t. with  $PCl_5$  see indic. refs.; for formn. of  $\bar{C}$  from 1,3,5-trichloro-

## 3:9351 DIMETHYL CHLOROMALEATE



Beil. II —

 $\text{H}_1$ -(305) $\text{H}_2$ -(646)

B.P. 106.5° cor. at 18 mm. (1)

$D_{4}^{25} = 1.2775$  (1)

100° at 17 mm. (2)

$D_{4}^{20} = 1.276$  (2)

$n_{\text{H}_2\text{O}}^{20} = 1.461$  (2)

$D_{4}^{18.9} = 1.2775$  (2)  $n_{\text{H}_2\text{O}}^{18.9} = 1.46170$  (2)

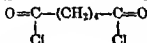
[For prepn. of  $\bar{\text{C}}$  from chloromaleic anhydride (3:0280) with abs. MeOH + conc.  $\text{H}_2\text{SO}_4$  in cold see (2).]

3:9351 (1) Walden, Swinne, *Z. physik. Chem.* 79, 741 (1912). (2) von Auwers, Harra, *Ber.* 62, 1681, 1686-1687 (1929).

## 3:9352 ADIPYL (DI)CHLORIDE



Beil. II - 653

 $\text{H}_1$ -(277) $\text{H}_2$ -(575)

B.P. 130-132° at 18 mm., sl. dec. (1)

125-128° at 11 mm., sl. dec. (1)

125° at 11 mm. (2)

83-85° at 1 mm. (3)

[For prepn. of  $\bar{\text{C}}$  from adipic acid (1:0775) with  $\text{PCl}_5$  (5) (yield: 79% (4), 50% (1)), with  $\text{PCl}_5$  (5) (82% yield (6)), with  $\text{PCl}_5$  +  $\text{ZnCl}_2$  (76% yield (4)), or with  $\text{SOCl}_2$  (yield: 100% (2), 90% (3), 81% (4), 60% (7)) (8) (9) (10) (19) see indic. refs.]

[For study of reactn. of  $\bar{\text{C}}$  with  $\text{Cl}_2$  see (11); of  $\bar{\text{C}}$  with  $\text{Br}_2$  see (11) (12) (13) (19); with diethyl sodio-malonate see (14); with  $\text{MeZnI}$  or  $\text{EtZnI}$  see (7); with triethylamine or with pyridine in  $\text{C}_6\text{H}_6$  see (15).]

[ $\bar{\text{C}}$  with  $\text{AlCl}_3$  +  $\text{C}_6\text{H}_6$  gives (75-81% yield (9)) (8) (1) (6) (16) 1,6-diphenylhexanedi-one-1,6 (dibenzoylbutane) [Beil. VII-777, VII-404], cryst. from alc., m.p. 106-107° (9), 107° (6) (16) (note that some  $\delta$ -benzoyl- $n$ -valeric acid [Beil. XI-339], m.p. 78° (16) 77-78° (17) ( $p$ -nitrophenylhydrazones, m.p. 187° (17), semicarbazones, m.p. 187° (17)), is, also formed). — For reactn. of  $\bar{\text{C}}$  with  $\text{AlCl}_3$  + toluene,  $m$ -xylene,  $p$ -xylene, mesitylene, (18) or chlorobenzene (8) see indic. refs.]

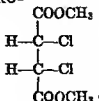
$\bar{\text{C}}$  on hydrolysis yields adipic acid (1:0775) (for the diamide, dianilide, di- $p$ -toluidide, and other derivs. corresp. to  $\bar{\text{C}}$  see 1:0775).

3:9352 (1) Etai, *Ann. chim.* (7) 9, 369-377 (1896). (2) Fröschl, Maier, *Monatsh.* 59, 271-272 (1928). (3) Lieser, Macura, *Ann.* 548, 226-251 (1911). *C.A.* 37, 4699 (1913). (4) Clark, *Beil. Trans. Roy. Soc. Can.* (3) 27, 111 97-103 (1933). (5) Ruggli, *Ann.* 399, 179-180 (1913). (6) Borsche, Wollemann, *Ber.* 45, 3715-3716 (1912). (7) Blaise, Koehler, *Bull. soc. chim.* (4) 5, 623 (1909).

— DIMETHYL *d,l*- $\alpha,\alpha'$ -DICHLORO-SUCCINATE

 $C_6H_8O_4Cl_2$ 

Beil. II —

II<sub>1</sub>-(267)II<sub>2</sub>-(557)

B.P. 116.5–120.5° cor. at 12.5 mm.

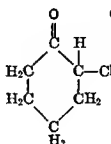
M.P. 43°

See 3:0485. Division A: Solids.

— 2-CHLOROCYCLOHEXANONE

 $C_6H_9OCl$ 

Beil. VII - 10

VII<sub>1</sub>-( 8)

B.P. 88–90° at 16 mm.

M.P. 23–24°

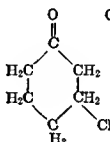
 $D_{15}^{20} = 1.161$  $n_D^{20} = 1.4825$ 

See 3:0120. Division A: Solids.

3:9360 3-CHLOROCYCLOHEXANONE

 $C_6H_9OCl$ 

Beil. VII-10



B.P. 91–92° at 14 mm. (1).

Colorless oil. —  $\bar{C}$  does not fume in air or attack skin (1).

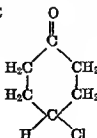
[For prepn. from cyclohexen-1-one-3 + dry HCl in dry ether see (1).]

3:9360 (1) Kötze, Grethe, *J. prakt. Chem.* (2) 80, 503–504 (1909).

3:9364 4-CHLOROCYCLOHEXANONE

 $C_6H_9OCl$ 

Beil. S.N. 612



B.P. 95° at 17 mm. (1)

 $n_D^{20} = 1.4867$  (1)

Liq. with penetrating odor (1).

[For prepn. from 4-chlorocyclohexanol-1 (3:9376) by oxidn. with  $\text{CrO}_3$  see (1) (3).]

④ 4-Chlorocyclohexanone-1 semicarbazone: From  $\bar{C}$  + semicarbazide HCl + KOAc (1); cryst. from aq., m p. 191° (block) (1); 196° (2).

3:9364 (1) Sabetay, Palfray, *Bull. soc. chim.* (4) 43, 909 (1928). (2) Palfray, Rothstein, *Compt. rend* 190, 944 (1930). (3) Backer, Tamsma, *Rec. trav. chim.* 57, 1205-1206 (1938).

3:9368 ETHYL  $\alpha$ -CHLOROISOCROTONATE  $C_6H_9O_2Cl$  Beil. II —  

$$\begin{array}{c} CH_3-C-H \\ \parallel \\ C_2H_5OOC-C-Cl \end{array}$$
 II<sub>1</sub>—  
 II<sub>2</sub>-(390)

B.P. 75° at 30 mm. (1)

$D_4^{20} = 1.100$  (1)  $n_D^{20} = 1.4530$  (1)

58° at 12 mm. (1)

$D_4^{18} = 1.1021$  (1)

[See also ethyl  $\alpha$ -chlorocrotonate (3:8523).]

[For prepn. of  $\bar{C}$  from Ag salt of  $\alpha$ -chloroisocrotonic acid (3:1615) with  $C_2H_5I$  see (1); note that attempts to prepare  $\bar{C}$  from  $\alpha$ -chloro-isocrotonic acid (3:1615) in EtOH with conc.  $H_2SO_4$  at 100° give only (1) the stereoisomeric ethyl  $\alpha$ -chlorocrotonate (3:8523).]

$\bar{C}$  with alc. KOH at room temp. gives upon acidification  $\alpha$ -chloroisocrotonic acid (3:1615), m p. 66°.

3:9368 (1) von Auwers, *Ann.* 432, 61-62 (1923)

3:9372 *sec*-BUTYL TRICHLOROACETATE  $C_6H_9O_2Cl_3$  Beil. S.N. 100  

$$\begin{array}{c} CH_3CH_2CH O.CO.CCl_3 \\ | \\ CH_3 \end{array}$$

B.P. 88-89° at 19 mm. (1)

$D_4^{25} = 1.252$  (1)  $n_D^{25} = 1.4440$  (1)

[For prepn. (82-89% yield) from butanol-2 (1:6155) + trichloroacetic ac. (3:1150) see (1).]

[For study of chlorination of  $\bar{C}$  see (1).]

3:9372 (1) Waddle, Adkins, *J. Am. Chem. Soc.* 61, 3361-3364 (1939).

— *ter*-BUTYL TRICHLOROACETATE  $C_8H_{17}O_2Cl_3$  Beil. S.N. 100  

$$Cl_3C.CO O C_4H_9$$

B.P. 37° at 1 mm.

M.P. 25.5°

$D_4^{25} = 1.2363$

$n_D^{25} = 1.4398$

See 3:9138. Division A: Solids.

3:9373 METHYL  $\gamma$ -(CHLOROFORMYL)-*n*-BUTYRATE  $C_6H_9O_2Cl$  Beil. S.N. 172  

$$\begin{array}{c} \gamma\text{-(Carbomethoxy)-}n\text{-butyryl chloride} \\ CH_3-CH_2-COOCH_3 \\ | \\ CH_3-C-Cl \\ || \\ O \end{array}$$

B.P. 110° at 30 mm. (1)

110-113° at 23 mm. (5)

110° at 20 mm. (2)

Note that  $\bar{C}$  is both an acid chloride and an ester.



.; [For prepn. of  $\bar{C}$  from methyl hydrogen glutarate [Beil. II<sub>2</sub>-(565)] (h.p. 158° at 27 mm. (1), 153° at 20 mm. (2), 150-151° at 10 mm. (3),  $D_{15}^{25} = 1.164$  (3),  $n_D^{18} = 1.4392$  (3), itself obtd. from glutaric anhydride with MeOH (2) (1) with  $\text{SOCl}_2$  at 20° for 12 hrs., then at 30° for 3 hrs. (yield 93% (1), 87% (5)) (2), see indic. refs.)]

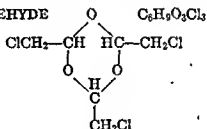
[For behavior of  $\bar{C}$  with  $\text{EtMgI}$  in toluene followed by hydrolysis giving  $\delta$ -keto-*n*-heptanoic acid, m.p. 50° see (2); for reaction of  $\bar{C}$  with atoxyl see (1).]

[For use of  $\bar{C}$  in Friedel-Crafts type of reaction see (4).]

[ $\bar{C}$  on catalytic hydrogenation as directed gives (70-85% yield (5)) methyl  $\gamma$ -formyl *n*-butyrate, b.p. 100-103° at 23 mm. (corresp. 2,4-dinitrophenylhydrazones, m.p. 105-106°) (5).]

3:9373 (1) Morgan, Walton, *J. Chem. Soc.* 1932, 277. (2) Clutterbuck, Raper, *Biochem. J.* 19, 393-394 (1925). (3) Fournau, Sabetay, *Bull. soc. chim.* (4) 45, 838-839 (1929). (4) Robinson, Walker, *J. Chem. Soc.* 1937, 62, 66-67. (5) Harris, Wolf, Mozingo, Arth, Anderson, Easton, Folkers, *J. Am. Chem. Soc.* 67, 2098 (1945).

# TRICHLOROPARALDEHYDE



$\text{C}_6\text{H}_9\text{O}_3\text{Cl}_3$

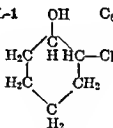
Beil. XIX - 386  
XIX<sub>1</sub>-(807)

B.P. 142° at 10 mm.

M.P. 87-87.5° cor.

See 3:2300. Division A: Solids

# 3:9374 *cis*-2-CHLOROCYCLOHEXANOL-1 (*cis*-Cyclohexene chlorohydrin)



$\text{C}_6\text{H}_{11}\text{OCl}$

Beil. S.N. 502

B.P. 93-94° at 26 mm. (1)

$D_{15}^{25} = 1.1261$  (1)  $n_D^{25} = 1.4860$  (1)

76° at 15 mm. (2)

$D_{15}^{15} = 1.150$  (2)  $n_D^{15} = 1.4860$  (2)

[See also *trans*-2-chlorocyclohexanol-1 (3:0175).]

[For prepn. of  $\bar{C}$  from 2-chlorocyclohexanone-1 (3:0120) by reductn. with isopropyl  $\text{MgCl}$ , *ter*-butyl  $\text{MgX}$ , or cyclohexanyl  $\text{MgX}$  (the prod. is actually a mixt. of  $\bar{C}$  (72-73%) with the *trans* isomer (27-28%) see (1); for formn. of  $\bar{C}$  from cyclohexene (1:8070) with  $\text{HOCl}$  see (2) cf. (5) (this method is claimed by (2) to yield some  $\bar{C}$ , but according to (1) gives solely the *trans* isomer).]

$\bar{C}$  with aq.  $\text{NaOH}$  gives on refluxing (76% yield (1)) cyclohexanone (1:5465) (note difference from the *trans* isomer which gives cyclohexene oxide). —  $\bar{C}$  with conc.  $\text{HCl}$  or with  $\text{ZnCl}_2$  in ether shows no tendency to convert to the *trans* isomer (1).

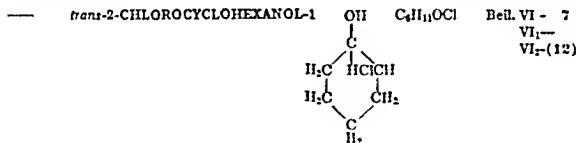
(Note: the following derivatives are listed as *trans* on the assumption of inversion during formation.)

— *trans*-2-Chlorocyclohexanyl acetate: const. not reported (4).

— *trans*-2-Chlorocyclohexanyl *N*-phenylurethane: m.p. 56-59° (3). [From  $\bar{C}$  + phenyl isocyanate in li. pet. (3)]

— *trans*-2-Chlorocyclohexanyl *N*-( $\alpha$ -naphthyl)carbamate: m.p. 165° (1). [From  $\bar{C}$  with  $\alpha$ -naphthyl isocyanate htd. 4 hrs. at 100° (1)]

3:0374 (1) Bartlett, *J. Am. Chem. Soc.* 57, 221-227 (1935). (2) Godchot, Mousseron, Granger, *Compt. rend.* 200, 715-740 (1935). (3) Cook, Hewitt, Lawrence, *J. Chem. Soc.* 1936, 75. (4) Winstein, Buckles, *J. Am. Chem. Soc.* 65, 616 (1943). (5) Newman, Van der Werf, *J. Am. Chem. Soc.* 67, 235 (1945).

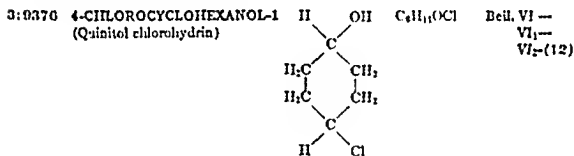


B.P. 104-106° at 45 mm.

M.P. 29°

$D_4^{15} = 1.140$   $n_D^{15} = 1.4850$

See 3:0175. *Duiron* 1. *Solids*.



B.P. 106° at 14 mm. (1)

105° at 12 mm. (2)

$D_4^{17} = 1.1435$  (2)  $n_D^{17} = 1.4930$  (2)

Colorless oil.

[For prepn. from quinitol (cyclohexanol-1,4) (Beil. VI-74) by htg. with conc. HCl see (1) (2); for formn. from resoritol (cyclohexanol-1,3) (Beil. VI-740) with conc. HCl see (1)]

[ $\bar{C}$  on refluxing 2 days in dry ether with Na yields (3) (by loss of HCl and rearr.) cyclohexanol-1, b.p. 67-68° at 14 mm.,  $D_4^{20} = 0.9125$ ,  $n_D^{20} = 1.4627$ ; *N*-phenylcarbamate, m.p. 82° (dark) (1)] — [ $\bar{C}$  with powd. KOH in ether is only partially transformed to cyclohexanol-1, even on boiling (1)]

$\bar{C}$  on oxida. with  $CrO_3$  yields (1) (3) 4-chlorocyclohexanone-1 (3:0364)

[Methyl deriv. of  $\bar{C}$  is an oil, b.p. 111-112° cor. at 18 mm.,  $D_4^{15.5} = 1.1282$ ,  $n_D^{15.5} = 1.4650$  (2)]

3:0376 4-Chlorocyclohexyl *N*-phenylcarbamate: m.p. 99° (2)

3:0376 (1) Fawcett, Fawcett, *Proc. Roy. Soc. (A)* 43, 978-990 (1928). (2) Fawcett, H. G. Fawcett, *Compt. rend.* 149, 501-503 (1929). (3) Fawcett, H. G. Fawcett, *Compt. rend.* 190, 542-545 (1930).

3:9380 *n*-AMYL CHLOROFORMATE  $C_5H_{11}O_2Cl$  Beil. S.N. 199  
 (*n*-Amyl chlorocarbonate)  $n-C_5H_{11}O.CO.Cl$

B.P. 60-62° at 15 mm. (1)

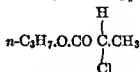
$n_D^{18} = 1.4181$  (2)

53.4-54.5° at 11 mm. (2)

$\bar{C}$  on htg. with quinoline dec. at 72° (3) into *n*-amyl chloride (3:7460) +  $CO_2$ ;  $\bar{C}$  on btg with  $ZnCl_2$  gives these + amylene (and its polymers) +  $HCl$  (4).

3:9380 (1) Eastman Organic Chemicals, List No. 36 (1946). (2) Kohlrausch, Sabathy, *Monatsh.* 72, 307 (1939). (3) Carré, *Bull. soc. chim.* (5) 3, 1069 (1936). (4) Underwood, Baril, *J. Am. Chem. Soc.* 57, 2729 (1935).

3:9384 *n*-PROPYL *d,l*- $\alpha$ -CHLOROPROPIONATE  $C_6H_{11}O_2Cl$  Beil. S.N. 162



B.P. —

$D_4^{20} = 1.0478$  (1)  $n_D^{20} = 1.4218$  (1)

3:9384 (1) Schjanberg, *Z. physik. Chem. A-172*, 230 (1935).

3:9388 ISOPROPYL  $\beta$ -CHLOROPROPIONATE  $C_6H_{11}O_2Cl$  Beil. S.N. 162  
 $(CH_3)_2CH.O.CO.CH_2.CH_2.Cl$

B.P. —

$D_4^{20} = 1.0503$  (1)  $n_D^{20} = 1.4230$  (1)

3:9388 (1) Schjanberg, *Z. physik. Chem. A-172*, 231 (1935).

3:9390  $\beta$ -( $\beta$ -HYDROXYETHOXY)ETHYL CHLOROACETATE Beil. S.N. 160  
 (Diethylene glycol mono(chloroacetate))  $C_6H_{11}O_4Cl$   
 $HOCH_2.CH_2.O.CH_2.CH_2.O.CO.CH_2Cl$

B.P. 130-142° at 0.2 mm. (1)

Viscous oil, insol in aq. but slowly dissolving when shaken with aq. because of hydrolysis to diethylene glycol (1:6525) + chloroacetic ac. (3:1370) (1).

3:9390 (1) Meerwein, Sönke, *J. prakt. Chem.* (2) 137, 317 (1933).

3:9394 FORMALDEHYDE  $\beta,\beta'$ -DICHLORO-  $C_6H_{12}O_2Cl_2$  Beil. I —  
 ISOPROPYL-ETHYL-ACETAL  $(ClCH_2)_2CH.O.CH_2.O.C_2H_5$  I<sub>1</sub>—  
 ( $\beta,\beta'$ -Dichloroisopropyl-ethyl-formal) I<sub>2</sub>-(640)

B.P. 96-98° at 15 mm. (1)

$D_{17}^{17} = 1.182$  (2)  $n_D^{17} = 1.44912$  (2)

90-91° at 12 mm. (2)

Colorless liq. with ethereal odor.

[For prepn. of  $\bar{C}$  from epichlorohydrin (3-chloro-1,2-epoxypropane) (3:5358) + chloromethyl ethyl ether (3:7195) see (1) (2).]

3:9394 (1) Blanchard, *Bull. soc. chim.* (4) 39, 1265 (1926). (2) Blanchard, *Bull. soc. chim.* (4) 49, 285 (1931).

3:9395 6-CHLOROHEXANOL-1  $\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{OH}$   $\text{C}_6\text{H}_{13}\text{OCl}$  Beil. S.N. 24  
( $\omega$ -Chloro-*n*-hexyl alcohol)  $\begin{array}{c} | \\ \text{Cl} \end{array}$

B.P. 116-117° at 19 mm. (1)

112° at 17 mm. (1)

[For prepn of  $\bar{\text{C}}$  from  $\alpha, \omega$ -hexamethylene glycol [Beil. I-484, I<sub>1</sub>-(251), I<sub>2</sub>-(551)] (b.p. 145-149° at 18 mm. (2)) with conc. HCl as directed (1) cf. (2) (yields: 65% (3)) see indic. refs.]

[ $\bar{\text{C}}$  with KSEt in alc. htd.  $\frac{1}{2}$  hr. gives (1) ethyl 6-hydroxy-*n*-hexyl sulfide, colorless oil, b.p. 134-136° at 17 mm.; this prod. with  $\text{SOCl}_2$  + diethylaniline in  $\text{CCl}_4$  at 55° gives (1) 6-chloro-*n*-hexyl ethyl sulfide, b.p. 128-131° at 26 mm.]

$\bar{\text{C}}$  with thiophenol has not been studied [however, 6-chloro-*n*-hexyl acetate with excess thiophenol in aq. NaOH htd. 3 hrs. gives (85% yield (2)) 6-hydroxy-*n*-hexyl phenyl sulfide, pl. from lt. pet., m.p. 43°; this prod. with  $\text{SOCl}_2$  + diethylaniline in  $\text{CCl}_4$  yields (2) 6-chloro-*n*-hexyl phenyl sulfide, m.p. 7-8° (undistillable)]

[ $\bar{\text{C}}$  (1 mole) with  $\text{Et}_2\text{NH}$  (2 moles) in s.t. at 100° for 16 hrs gives (58% yield (4)) 6-(diethylamino)hexanol-1, b.p. 96-99° at 2 mm. (4), this prod. with  $\text{SOCl}_2$  in  $\text{CHCl}_3$  gives (39% yield (4)) 6-(diethylamino)-*n*-hexyl chloride, b.p. 118-120° at 19 mm.]

$\bar{\text{C}}$  with morpholine gives (5) alm. quant. 6-(4-morpholinyl)hexanol-1, b.p. 146.0-147.0° at 5 mm.,  $D_4^{25} = 0.9884$ ,  $n_D^{25} = 1.4750$  (corresp. *N*-( $\alpha$ -naphthyl)carbamate, m.p. 71.0-72.0° cor.) (5). —  $\bar{\text{C}}$  (1 mole) with *N*-phenylpiperazine (2 moles) at 100° for 5 hrs gives (3) in alm. 100% yield (as salt) *N*-(6-hydroxy-*n*-hexyl)-*N'*-phenylpiperazine, m.p. 65.5-67.0° cor. (corresp. *N*-phenylcarbamate, m.p. 91.5-93.0° cor.) (3).

—6-Chloro-*n*-hexyl acetate: oil, b.p. 113-116° at 17 mm [Prepd. indirectly (2)]

Ⓐ 6-Chloro-*n*-hexyl *N*-phenylcarbamate: m.p. 49-50° (3).

3:9395 (1) Bennett, Turner, *J. Chem. Soc.* 1938, 813-815 (2) Bennett, Mosses, *J. Chem. Soc.* 1931, 1698-1699. (3) Anderson, Pollard, *J. Am. Chem. Soc.* 61, 3439-3440 (1939). (4) Work, *J. Chem. Soc.* 1942, 428. (5) Anderson, Pollard, *J. Am. Chem. Soc.* 61, 3440-3441 (1939).

3:9306 *n*-BUTYL  $\alpha$ -CHLOROETHYL ETHER  $\begin{array}{c} \text{H} \\ | \\ \text{CH}_3 - \text{C} - \text{O} - \text{C}_4\text{H}_9 \\ | \\ \text{Cl} \end{array}$   $\text{C}_6\text{H}_{13}\text{OCl}$  Beil. S.N. 78  
( $\alpha$ -Chloroethyl *n*-butyl ether)

B.P. 48.9-50.3° cor. at 11 mm. (1)

$D_4^{20} = 0.0335$  (1)  $n_D^{20} = 1.4155$  (1)

$\bar{\text{C}}$  decomposes considerably if distd. at ord. press. (2).

[For prepn. (95% yield (1)) from paraldehyde (1:0170) + *n*-butyl alc. (1:6180) + dry HCl see (1).]

$\bar{\text{C}}$  on stdg. polymerizes to dark tarry residue (1).

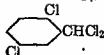
[ $\bar{\text{C}}$  on bromination yields  $\alpha, \beta$ -dibromoethyl *n*-butyl ether (2).]

$\bar{\text{C}}$  on shaking with aq. yields acetaldehyde (1:0100), *n*-butyl alc. (1:6180), + HCl.

3:9396 (1) Henze, Murchison, *J. Am. Chem. Soc.* 53, 4077-4079 (1931). (2) Dykstra, Lewis, Boord, *J. Am. Chem. Soc.* 52, 3399-3400 (1930).

2,5-DICHLOROBENZAL (DI)CHLORIDE  $C_7H_4Cl_4$ 

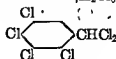
Beil. V - 302

V<sub>1</sub>—V<sub>2</sub>—(234)

B.P. 118–120° at 14 mm.

M.P. 43°

See 3:0490. Division A: Solids.

3:9397 2,3,4,5-TETRACHLOROBENZAL (DI)CHLORIDE  $C_7H_2Cl_6$  Beil. S.N. 466No physical constants on  $\bar{C}$  are available.[For prepn. of  $\bar{C}$  from 2,3,4,5-tetrachlorotoluene (3:2710) with  $Cl_2$  see (1).] $\bar{C}$  on hydrolysis (presumably with strong  $H_2SO_4$ ) gives (1) 2,3,4,5-tetrachlorobenzaldehyde (3:3140).

3:9397 (1) Chem. Fabrik Griesheim-Elektron, Brit. 251,511, May 27, 1926; Cent. 1926, II 2355; C.A. 21, 1361 (1927); French 603,650, April 26, 1926; Cent. 1926, II 2355; not in C.A.

## 3:9398 2,6-DICHLOROBENZAL (DI)CHLORIDE

 $C_7H_4Cl_4$ 

Beil. V - 302

V<sub>1</sub>—V<sub>2</sub>—

B.P. 124–126° at 16 mm. (1)

Oil with penetrating odor.

[For prepn. of  $\bar{C}$  from 2,6-dichlorobenzaldehyde (3:1690) with  $PCl_5$  (90% yield (1)) (2) (note the intermediate formn. of bis-( $\alpha$ ,2,6-trichlorobenzyl) ether, (2)) or from 2,6-dichlorotoluene (3:6270) with  $Cl_2$  (4) see indic. refs.] $\bar{C}$  is extremely resistant to hydrolysis with either acid or alkali or conc.  $H_2SO_4$ ; for details see (3) (5).[For condens. of  $\bar{C}$  with various phenols (e.g., 2,4-dichlorophenol (3:0560)) in prepn. of mothproofing agts. see (6).]

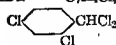
3:9398 (1) Z. Naturforsch. Monatsh. 58, 157, 160 (1933).  
 -him. 52,  
 53, Ger.  
 (1933).  
 4, 1930;

French 39,334, Oct. 12, 1931, Cent. 1932, I 3013.

## 3:9399 2,4-DICHLOROBENZAL (DI)CHLORIDE

 $C_7H_4Cl_4$ 

Beil. S.N. 466



This compound appears to be unreported. However, for many isomeric compounds see the Formula Index.

3:9402 5-CHLORO-5-METHYLHEXEN-1-YNE-3  $C_7H_9Cl$  Beil. S.N. 13  
 (2-Chloro-2-methylhexen-5-yne-3;  
 dimethyl-vinylethynyl-carbinyl  
 chloride)  $CH_2=CH-C\equiv C-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

B.P. 48-49° at 28 mm. (1)

$n_D^{15} = 1.4812$  (1)

31-32° at 10 mm. (1)

[For prepn. of  $\bar{C}$  from dimethyl-vinylethynyl-carbinol (b.p. 58-59° at 13 mm,  $D_4^{15} = 0.8925$ ,  $n_D^{15} = 1.4786$  (2), see (1).]

[ $\bar{C}$  with phenol + KOH in acetone refluxed 3 hrs. yields (3) about equal amts. of 2-methylhexadien-1,5-yne-3 ( $\alpha$ -isopropenyl- $\beta$ -vinyl-acetylene) + the phenyl ether of  $\bar{C}$  (dimethyl-phenoxy-vinylethynyl-methane), b.p. 105.5° at 7 mm.,  $D_4^{16} = 0.9714$ ,  $n_D^{15} = 1.5350$  (3).]

3:9402 (1) Nazarov, *Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Ser. chim.* 1938, 695-705; *Cent.* 1939, II 3403; *C.A.* 33, 5682 (1939). (2) Nazarov, *Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Ser. chim.* 1938, 683-694; *Cent.* 1939, II 3402; *C.A.* 33, 5682 (1939). (3) Nazarov, Elizarova, *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1941, 423-430; *C.A.* 36, 1298 (1942).

3:9406 1-CHLORO-3-ETHYLPENTADIENE-1,2  $C_7H_{11}Cl$  Beil. S.N. 12  
 $CH_3CH_2-\overset{\overset{Cl}{|}}{C}=\overset{\underset{\underset{C_2H_5}{|}}{C}}{C}=CH$

B.P. 85-88° at 100 mm. (1)

$D_4^{18.5} = 0.9297$  (1)  $n_D^{18.5} = 1.47036$  (1)

$D_4^{16.5} = 0.9329$  (1)  $n_D^{16.5} = 1.48431$  (1)

[For prepn. of  $\bar{C}$  from 3-ethylpentyn-1-ol-3 (diethyl-ethynyl-carbinol) [Beil. I<sub>1</sub>-(236), I<sub>2</sub>-(506)] (1) directly, or from the intermediate 1-chloro-3-ethylpentyn-1 (3:9410) by rearr., on shaking either with aq. HCl contg.  $Cu_2Cl_2$  +  $NH_4Cl$  (some 3-ethylpenten-3-yne-1 also being formed in the latter case) see (1).]

$\bar{C}$  with nq. +  $CaCO_3$  first isomerizes to 1-chloro-3-ethylpentyn-1 (3:9410) which then yields 3-ethylpentyn-1-ol-3 (b.p. 136-137°,  $D_4^{17} = 0.8748$ ; *N*-phenylcarbamate, m.p. 52-53° (1); allophanate, m.p. 130-131° (2)) and 3-ethylpenten-3-yne-1, b.p. 41-43° at 100 mm,  $D_4^{13} = 0.7733$ ,  $n_D^{13} = 1.43962$ ,  $n_D^{15} = 1.45224$  (1).

3:9406 (1) T. A. Favorskaya, I. A. Favorskaya, *J. Gen. Chem. (U.S.S.R.)* 10, 451-460 (1940); *C.A.* 34, 7844 (1940). (2) Locquin, Sung, *Bull. soc. chim.* (4) 33, 601 (1924).

3:9410 1-CHLORO-3-ETHYLPENTYNE-1  $C_7H_{11}Cl$  Beil. S.N. 12  
 $CH_3CH_2-\overset{\underset{\underset{C_2H_5}{|}}{CH}}{C}-\overset{\overset{Cl}{|}}{C}\equiv C$

B.P. 73-76° at 100 mm. (1)

$D_4^{18.5} = 0.0230$  (1)  $n_D^{18.5} = 1.44372$  (1)

$D_4^{16.5} = 0.9330$  (1)  $n_D^{16.5} = 1.45364$  (1)

[For prepn. of  $\bar{C}$  from 3-ethylpentyn-1-ol-3 (diethyl-ethynyl-carbinol) [Beil. I<sub>1</sub>-(236), I<sub>2</sub>-(506)] (1) on shaking with HCl alone, or with HCl +  $Cu_2Cl_2$  +  $NH_4Cl$  (70% yield together in the latter case with a maximum of 25-30% 1-chloro-3-ethylpentadiene-1,2 (3:9406)) see (1).]

$\bar{C}$  on shaking with  $HCl + Cu_2Cl_2 + NH_4Cl$  is partly converted to 1-chloro-3-ethylpentadiene-1,2 (3:9406) (some 3-ethylpenten-3-yne-1 also being formed), but without the  $HCl$  no action occurs (1).

$\bar{C}$  easily loses  $HCl$  yielding 3-ethylpenten-3-yne-1, b.p.  $41-43^\circ$  at 100 mm.,  $D_4^{13} = 0.7733$ ,  $n_D^{13} = 1.43962$ ,  $n_D^{14} = 1.45224$  (1).

$\bar{C}$  upon hydrolysis (1) with aq.  $+ CaCO_3$  gives a mixt. of 3-ethylpentyn-1-ol-3 (b.p.  $136-137^\circ$ ,  $D_4^{17} = 0.8748$ ,  $n_D^{14} = 1.4385$ ,  $n_D^{14} = 1.44697$  (1) [N-phenylcarbamate, m.p.  $52-53^\circ$  (1), allophanate, m.p.  $130-131^\circ$  (2)]) and 3-ethylpenten-3-yne-1 (see above).

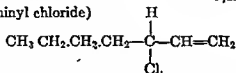
3:9410 (1) T. A. Favorskaya, I. A. Favorskaya, *J. Gen. Chem. (U.S.S.R.)* 10, 451-460 (1940); *C.A.* 34, 7844 (1940). (2) Locquun, Sung, *Bull. soc. chim.* (4) 35, 601 (1924).

### 3:9412 *d,l*-3-CHLOROHEPTENE-1

 $C_7H_{13}Cl$ 

Beil. S.N. 11

(n-Butyl-vinyl-carbinyl chloride)



$\bar{C}$  as such is as yet unreported, but both of the opt. active stereoisomerides have been prepared.

[The dextrorotatory isomer, b.p.  $92-94^\circ$  at 125 mm. (1),  $87-88^\circ$  at 90 mm. (1),  $D_4^{25} = 0.8857$  (1), has been obtd. from levorotatory hepten-1-ol-3 (n-butyl-vinyl-carbinol) [Beil. I<sub>2</sub>(488)] with  $PCl_5$  in dry ether (1), with  $PCl_5 +$  pyridine (2), or from levorotatory 3-bromoheptene-1 (1) with  $LiCl$  in  $MeOH$  (1).

[Upon ozonolysis in  $CHCl_3$  followed by  $Br_2/aq.$  oxidn. of the resultant aldehyde, levorotatory  $\alpha$ -chlorocaproic acid, b.p.  $80-95^\circ$  at 1 mm., was obtd. (2).]

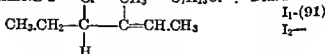
[The levorotatory isomer, b.p.  $87-90^\circ$  at 92 mm. (3),  $D_4^{25} = 0.8883$  (4),  $n_D^{25} = 1.4380$  (4), has been obtd. from dextrorotatory hepten-1-ol-3 (n-butyl-vinyl-carbinol) [Beil. I<sub>2</sub>(488)] with  $PCl_5$  (3); upon catalytic hydrogenation it yields (3) dextrorotatory 3-chloroheptane, b.p.  $87-90^\circ$  at 113 mm.,  $n_D^{25} = 1.4221$  (3); cf. *d,l*-isomer (3:8080).]

3:9412 (1) Levene, Rothen, Kuna, *J. Biol. Chem.* 120, 787-790 (1937). (2) Levene, Haller, *J. Biol. Chem.* 83, 597 (1929). (3) Levene, Rothen, *J. Biol. Chem.* 119, 191-192 (1937). (4) Levene, Rothen, *J. Chem. Phys.* 5, 981 (1937).

### 3:9414 4-CHLORO-3-METHYLHEXENE-2

 $C_7H_{13}Cl$ 

Beil. I—

I<sub>1</sub>-(91)I<sub>2</sub>—B.P.  $51^\circ$  at 11.5 mm. (1)

[For prepn. of  $\bar{C}$  from 3-methylhexen-2-ol-4 [Beil. I-447, I<sub>1</sub>-(229)] with 6 N  $HCl$  see (1).]

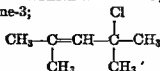
3:9414 (1) Abellmann, *Ber.* 43, 1581 (1910).

### 3:9418 4-CHLORO-2,4-DIMETHYLPENTENE-2

 $C_7H_{13}Cl$ 

Beil. S.N. 11

(2-Chloro-2,4-dimethylpentene-3; trimethylcrotyl chloride)



[ $\bar{C}$  is too unstable for purification by distillation; however, it can be prepared in solution from 2,4-dimethylpenten-3-ol-2 (1) with  $PCl_5$  in dry ether.]

benzene (3:1400) with  $\text{Cl}_2$  in pres. of  $\text{Al/Hg}$  see (11); from benzene (12), chlorobenzene (13), or diphenyl sulfone (14) with  $\text{Cl}_2$  followed by treatment with alc.  $\text{KOH}$  see indic. refs.] [For behavior of  $\bar{\text{C}}$  with liq.  $\text{Cl}_2$  yielding addn. products see (15).]

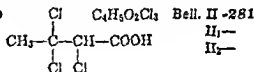
[For behavior of  $\bar{\text{C}}$  with  $\text{NaOMe}$  see (2) (16).]

$\bar{\text{C}}$  on mononitration, e.g., by boilg. for  $\frac{1}{2}$  hr. with 3 pts.  $\text{HNO}_3$  ( $D = 1.52$ ) as directed (17), gives 96.7% yield (17) 1,2,3,5-tetrachloro-4-nitrobenzene, cryst. from spontaneous evapn. of alc. soln., m.p. 40–41° (17) (the m.p. of 21–22° previously reported (5) was on impure material).

$\bar{\text{C}}$  on dinitration, e.g., by boilg. with a mixt. of 10 pts. fuming  $\text{HNO}_3$  ( $D = 1.52$ ) + 4 pts. conc.  $\text{H}_2\text{SO}_4$  for 1 hr. and then pouring into aq. (17), gives (100% yield (17)) (9) 1,2,3,5-tetrachloro-4,6-dinitrobenzene [Beil. V-266], pl. from 90%  $\text{AcOH}$ , m.p. 162° (9), 161–162° (17). (This prod. on htg. with aniline yields (9) (18) 2-chloro-1,3,5-trianilino-4,6-dinitrobenzene, crimson pl., m.p. 179° (9), 179–180° (18).)

3:0915 (1) Silberrad, *J. Chem. Soc.* 121, 1020 (1922). (2) Holleman, *Rec. trav. chim.* 39, 739, 749 (1920). (3) Willgerodt, Wileke, *Ber.* 43, 2752 (1910). (4) Olivier, *Rec. trav. chim.* 39, 197 (1920). (5) Beilstein, Kurbatow, *Ann.* 192 237–238 (1878). (6) Dadiou, Pongratz, Kohlrausch, *Monatsh.* 61, 433–434 (1932). (7) Schoutissen, *J. Am. Chem. Soc.* 55, 4539 (1933). (8) Gebauer-Fulnegg, Figdor, *Monatsh.* 48, 633–634 (1927). (9) Jackson, Carlton, *Ber.* 35, 395 (1908). (10) Molinoux, *Ann.* 415, 62 (1918). (11) Molinoux, *Ann.* 415, 62 (1918). (12) Molinoux, *Ann.* 415, 62 (1918). (13) Molinoux, *Ann.* 415, 62 (1918). (14) Otto, Ostrop, *Ann.* 141, 105 (1867). (15) van der Linden, *Rec. trav. chim.* 55, 421–439 (1936). (16) de Crauw, *Rec. trav. chim.* 50, 767 (1931). (17) Berekmans, Holleman, *Rec. trav. chim.* 44, 852–856 (1925). (18) Qvist, Salo, *Acta Acad. Aboensis Math. et Phys.* 8, No 4 (1934), *Cent.* 1934, II 505, *Cent.* 1936, I 540.

### 3:0925 $\alpha,\beta,\beta$ -TRICHLORO-*n*-BUTYRIC ACID



M.P. 51.5–52° (1)

This from lgr. — Spar. sol. aq., eas. sol. alc., ether,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ ,  $\text{CS}_2$ .

[For prepn. of  $\bar{\text{C}}$  from either  $\beta$ -chlorocrotonic acid (3:2625) or  $\beta$ -chloroisocrotonic acid (3:1300) in  $\text{CS}_2$  soln. with  $\text{Cl}_2$  stood several days in the dark see (1).]

[ $\bar{\text{C}}$  in aq. with granulated  $\text{Zn}$  stood for 6 weeks, then acidified, yields (1) mainly  $\beta$ -chloroisocrotonic acid (3:1300) accompanied by some  $\beta$ -chlorocrotonic acid (3:2625); note that former is separated from latter by its greater volatility with steam.]

$\bar{\text{C}}$  with aq.  $\text{Na}_2\text{CO}_3$  soln. on boilg. loses both  $\text{HCl}$  and  $\text{CO}_2$  yielding the higher-boilg. (1) 1,2-dichloropropene-1 (3:5150).

$\bar{\text{C}}$  with alc.  $\text{KOH}$  (2 moles) loses  $\text{HCl}$  yielding (1) mainly  $\alpha,\beta$ -dichloroisocrotonic acid [Beil. II-418], m.p. 75.5°, accompanied by a little  $\alpha,\beta$ -dichlorocrotonic acid [Beil. II-418], m.p. 92°; note that these are separated by the greater soly. of the former in lgr. (1).

The acid chloride corresp. to  $\bar{\text{C}}$  is unreported.

— Methyl  $\alpha,\beta,\beta$ -trichloro-*n*-butyrate: unreported.

— Ethyl  $\alpha,\beta,\beta$ -trichloro-*n*-butyrate: unreported.

—  $\alpha,\beta,\beta$ -Trichloro-*n*-butyramide: unreported.

—  $\alpha,\beta,\beta$ -Trichloro-*n*-butyranilide: unreported.

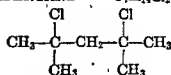
—  $\alpha,\beta,\beta$ -Trichloro-*n*-butyr- $\alpha$ -naphthalide: unreported.



[For prepn. of  $\bar{C}$  from heptanone-4 (butyrene) (1:5447) with  $\text{PCl}_5$  see (1); note that heptyne-3 (1:8095), b.p. 105–106°, and 4-chloroheptene-3 (3:8023) are also formed (1). The earlier prepn. are regarded as impure.]

3:9426 (1) Bourgeul, *Bull. soc. chim.* (4) 35, 1636–1637 (1924). (2) Bourgeul, *Ann. chim.* (10) 3, 372 (1925).

3:9428 2,4-DICHLORO-2,4-DIMETHYLPENTANE  $\text{C}_7\text{H}_{14}\text{Cl}_2$  Beil. S.N. 10

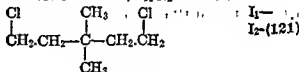


B.P. 51.5°, at 8 mm. (1)

[For study of behavior of  $\bar{C}$  with aq. alc.  $N/10$   $\text{NaOH}$  see (1).]

3:9428 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 9, 1380–1388 (1939); *C.A.* 34, 1611 (1940).

3:9430 1,5-DICHLORO-3,3-DIMETHYLPENTANE  $\text{C}_7\text{H}_{14}\text{Cl}_2$  Beil. I—



B.P. 135° at 80 mm. (1)  
58–59° at 8 mm. (2)

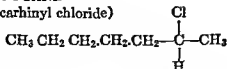
$D_4^{15} = 1.0917$  (2)  $n_D^{15} = 1.48990$  (2)

[For prepn. of  $\bar{C}$  from 3,3-dimethylpentanediol-1,5 (1) with  $\text{SOCl}_2$  refluxed for 4 hrs. (yield 80% (1)); from  $N$ -benzoyl-4,4-dimethylpiperidine (2) with  $\text{PCl}_5$  see (2).]

[For reactn. of  $\bar{C}$  with alc.  $\text{NaCN}$  giving (yield: 80% (2), 40% (1)) 3,3-dimethylpimelonitrile, cryst. from  $\text{C}_6\text{H}_6/\text{lgr.}$ , m.p. 123° (2), b.p. 155–157° at 7 mm. (1),  $D_4^{20} = 1.0936$  (1),  $n_D^{20} = 1.4404$  (1), see indic. refs.] [This dinitrile upon htg. with conc.  $\text{HCl}$  in s.t. 4 hrs. at 120° gives (85% yield (2))  $\gamma,\gamma$ -dimethylpimelic acid; ndls. from  $\text{C}_6\text{H}_6/\text{lgr.}$ , m.p. 83° (2) (diamide, m.p. 176° (2); dianilide, m.p. 165° (2)).]

3:9430 (1) Miller, Adams, *J. Am. Chem. Soc.* 55, 789 (1936). (2) Komppa, *Ber.* 62, 1371–1372 (1929).

3:9432 *d,l*-2-CHLOROHEPTANE  $\text{C}_7\text{H}_{15}\text{Cl}$  Beil. I-154  
(*n*-Amyl-methyl-carbinyl chloride)



B.P. 46.0° at 19.5 mm. (1)

$D_4^{20} = 0.8672$  (1)  $n_D^{20} = 1.4221$  (1)  
 $D_4^{15} = 0.8725$  (1)

[For prepn. from heptanol-2 (1:6235) with conc.  $\text{HCl} + \text{ZnCl}_2$  at 0° for 6–8 hrs. (60–64% yield (1)) see (1).]

$\bar{C}$  converted to corresp. acetate by 7-hr. reflux with  $\text{KOAc} + \text{AcOH}$ , then hydrolyzed by 6-hr. boilg. with 20% alc.  $\text{KOH}$ , and the resultant heptanol-2 oxidized with  $\text{CrO}_3/\text{H}_2\text{SO}_4$ , gives (1) heptanone-2 (1:5460), pptd. as the semicarbazone, m.p. 123° (1).

3:9432 (1) Sherrill, *J. Am. Chem. Soc.* 52, 1985–1983 (1930).

$\tilde{C}$  on attempted distillation gave (1) almost quantitative yields of 2,4-dimethylpentadiene-1,3 [Beil. I-257, I<sub>1</sub>-(121), I<sub>2</sub>-(235)], b.p. 92-93° (1).

[For reactn. of  $\tilde{C}$  with phenol + K<sub>2</sub>CO<sub>3</sub> in acetone see (1).]

3:9418 (1) Hurd, Cohen, *J. Am. Chem. Soc.* 53, 1920-1922 (1931).

3:9420 1,2-DICHLOROHEPTANE  $\begin{array}{c} \text{Cl} \quad \text{Cl} \\ | \quad | \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{CH}-\text{CH}_2 \end{array}$  C<sub>7</sub>H<sub>14</sub>Cl<sub>2</sub> Beil. S.N. 10

B.P. 68-72° at 7 mm. (1)  $D_4^{20} = 1.064$  (1)  $n_D^{20} = 1.4490$  (1)

[For prepn. of  $\tilde{C}$  from heptene-1 (1:8324) with Cl<sub>2</sub> in CCl<sub>4</sub> at -15° (13% yield (1)) or with SOCl<sub>2</sub> (30-40% yield (1)) see (1).]

$\tilde{C}$  passed over soda-lime at 420° (3% yield) or htd. to 250° with powdered KOH in mineral oil (33% yield) loses 2 HCl giving (1) *n*-amylacetylene (1:8085) accompanied by other prods.

3:9420 (1) Bachmann, Hill, *J. Am. Chem. Soc.* 56, 2730-2731 (1934).

3:9422 1,7-DICHLOROHEPTANE C<sub>7</sub>H<sub>14</sub>Cl<sub>2</sub> Beil. I-154  
(Heptamethylene dichloride)  $\begin{array}{c} \text{Cl} \quad \text{Cl} \\ | \quad | \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{CH}_2 \end{array}$  I<sub>1</sub>-  
I<sub>2</sub>-

B.P. 120° at 28 mm. (1)

[For prepn. of  $\tilde{C}$  (60% yield (1)) from *N,N'*-bis-benzoylheptamethylenediamine [Beil. IX-264] via conversion with PCl<sub>5</sub> to the corresp. bis-imidechloride and distillation of the latter see (1); for formn. of  $\tilde{C}$  (together with other prods.) from heptamethylenediamine [Beil. IV-271] + NOCl see (2).]

⑥ 1,7-Diphenoxyheptane (heptanediol-1,7 bis-phenyl ether) [Beil. VI-148]: colorless cryst. from hot alc., m.p. 53° (1), 54.5-55° (2). [From  $\tilde{C}$  on htg. with excess NaOC<sub>6</sub>H<sub>5</sub> in alc. (1) (2).]

3:9422 (1) von Braun, Müller, *Ber.* 38, 2347 (1905) (2) Ssolonina, *J. Russ. Phys.-Chem. Soc.* 30, 606-632 (1898); *Cent.* 1898, I 26.

3:9424 2,2-DICHLOROHEPTANE  $\begin{array}{c} \text{Cl} \\ | \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}-\text{CH}_3 \\ | \\ \text{Cl} \end{array}$  C<sub>7</sub>H<sub>14</sub>Cl<sub>2</sub> Beil. S.N. 10

B.P. 77° at 25 mm. (1)

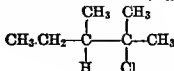
[For prepn. of  $\tilde{C}$  from heptanone-2 (*n*-amyl methyl ketone) (1:5460) with PCl<sub>5</sub> (23% yield accompanied by 40% yield of 2-chloroheptene-1 (3:7988)) see (1).]

3:9424 (1) Bachmann, Hill, *J. Am. Chem. Soc.* 56, 2730 (1934).

3:9426 4,4-DICHLOROHEPTANE  $\begin{array}{c} \text{Cl} \\ | \\ \text{CH}_3\text{CH}_2\text{CH}_2-\text{C}-\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{Cl} \end{array}$  C<sub>7</sub>H<sub>14</sub>Cl<sub>2</sub> Beil. I-154  
I<sub>1</sub>-  
I<sub>2</sub>-(117)

B.P. 86° at 27 mm. (1)  $D_4^{17} = 1.008$  (1)  $n_D^{17} = 1.448$  (1) (2)  
60.5° at 11 mm. (2) 1.006 (2)

3: 9442 *d,l*-2-CHLORO-2,3-DIMETHYLPENTANE  $C_7H_{16}Cl$  Beil. S.N. 10  
(*sec.*-Butyl-dimethyl-carbinyl  
chloride)



B.P. 38-39° at 20 mm. (1)

$n_D^{20} = 1.4264$  (1)

$\bar{C}$  has been obtd. (1) only as a by-product (10% yield) from the reactn. of 2,3-dimethyl-pentanol-2 with  $AlCl_3$  and  $C_6H_5$ ; the structure assigned above should be accepted with reserve.

3: 9442 (1) Huston, Fox, Binder, *J. Org. Chem.* 3, 253 (1939).

— 5-CHLORO-2-HYDROXYBENZALDEHYDE  $C_7H_5O_2Cl$  Beil. VIII-53  
VIII<sub>1</sub>—

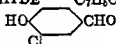


B.P. 105° at 12 mm.

M.P. 100°

See 3: 2800. Division A: Solids.

— 3-CHLORO-4-HYDROXYBENZALDEHYDE  $C_7H_5O_2Cl$  Beil. VIII-81  
VIII<sub>1</sub>—

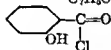


B.P. 149-150° at 14 mm.

M.P. 139° cor.

See 3: 4065. Division A: Solids.

— 2-HYDROXYBENZOYL CHLORIDE  $C_7H_5O_2Cl$  Beil. X—  
X<sub>1</sub>-(43)



B.P. 92° at 15 mm.

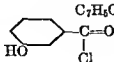
M.P. 19°

$D_D^{20} = 1.3112$

$n_D^{20} = 1.5812$

See 3: 0085. Division A: Solids.

3: 9446 3-HYDROXYBENZOYL CHLORIDE  $C_7H_5O_2Cl$  Beil. X—  
X<sub>1</sub>-(66)

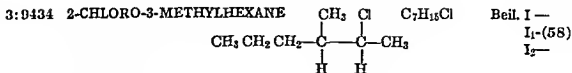


B.P. 110-113° at 0.5 mm. (1)

Pale yel. oil, not solidifying at -15° (2). —  $\bar{C}$  has odor and lachrymatory props. similar to benzoyl chloride; on stdg. even in s.t. turns brown and decomposes (1).

[For prepn. of  $\bar{C}$  from Na or K salts of *m*-hydroxybenzoic acid (1:0825) with  $SOCl_2$  (2) or with  $COCl_2$  in toluene (3) see indic. refs.]

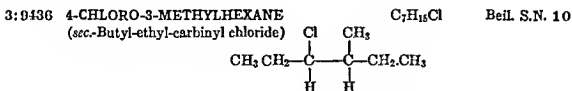
$\bar{C}$  with MeOH yields (1) methyl *m*-hydroxybenzoate (1:1468), m.p. 70°, h.p. 178° at 17 mm. (1);  $\bar{C}$  with EtOH yields (1) ethyl *m*-hydroxybenzoate (1:1471), m.p. 73.8°, h.p. 180° at 17 mm. (1);  $\bar{C}$  with dry  $NH_3$  gas in  $CHCl_3$  yields (1) *m*-hydroxybenzamide, lfts.



B.P. 53-58° at 36 mm. (1)

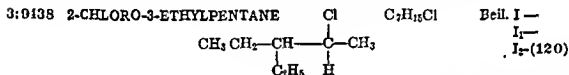
[For prepn. of  $\bar{\text{C}}$  (80% yield (1)) from 3-methylhexanol-2 [Beil.  $\text{I}_1$ -(206),  $\text{I}_2$ -(445)] with  $\text{PCl}_5$  see (1).]

3:9434 (1) Bjelouss, *Ber.* 45, 627-628 (1912).



Only a levorotatory isomer of  $\bar{\text{C}}$  has been reported; this resulted from treatment (1) of levorotatory 3-methylhexanol-4 (1) with  $\text{SOCl}_2$  in pet. ether; b.p. 37° at 15 mm. (1).

3:9436 (1) Duveen, Kenyon, *Bull. soc. chim.* (5) 5, 1120-1126 (1938).

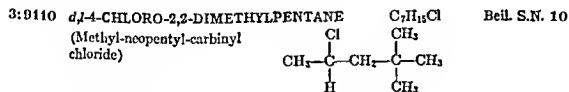


B.P. 62-62.5° cor. at 50 mm. (1)

$D_{25}^{25} = 0.8911$  (1)  $n_D^{25} = 1.4295$  (1)  
 $n_D^{20} = 1.4318$  (1)

[For prepn. of  $\bar{\text{C}}$  from 3-ethylpentanol-2 [Beil. I 416,  $\text{I}_1$ -(207),  $\text{I}_2$ -(445)] (1) with conc.  $\text{HCl} + \text{ZnCl}_2$  at room temp. in 35% yield see (1).]

3:9438 (1) Lucas, *J. Am. Chem. Soc.* 51, 252 (1929).



B.P. 03° at 250 mm. (1)  
 63-65° at 85 mm. (2)

$D_4^{20} = 0.855$  (1)  $n_D^{20} = 1.4180$  (1)  
 1.4183 (2)

[For prepn. of  $\bar{\text{C}}$  from 2,2-dimethylpentanol-4 (methyl-neopentyl-carbinol) satd. with dry  $\text{HCl}$  and stood 8 weeks (90% yield (1)) or treated with dry  $\text{HCl}$  under press. for 22 weeks (2) see indic. refs.]

$\bar{\text{C}}$  with  $\text{Mg}$  in dry ether gives  $\text{RMgCl}$ ; this on oxidn. with  $\text{O}_2$  yields (1) 2,2-dimethylpentanol-4, b.p. 136-136.5° at 730 mm. (2),  $n_D^{20} = 1.4183$  (2) (*N*-( $\alpha$ -naphthyl)carbamate, m.p. 84° (1)).

$\bar{\text{C}}$  converted to  $\text{RMgCl}$ , treated with  $\text{CO}_2$ , gives (50% yield (2)) isobutyl-neopentyl-acetic acid, b.p. 109° at 14 mm.,  $n_D^{20} = 1.4233$  (2) (amide, m.p. 123° (2); anilide, m.p. 117.5° (2)).

3:9440 (1) Whitmore, Johnston, *J. Am. Chem. Soc.* 60, 2267 (1938). (2) Whitmore, Noll, Heyd, *Samatiz, J. Am. Chem. Soc.* 63, 2023 (1941).

## 2,6-DICHLORO-4-METHYLPHENOL



Beil. VI - 403

VI<sub>1</sub>-(204)VI<sub>2</sub>—

B.P. 138-139° at 28 mm.

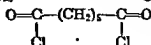
M.P. 38-39°

See 3:0400. Division A: Solids.

## 3:9450 PIMELYL (DI)CHLORIDE



Beil. II - 671

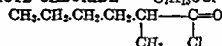
II<sub>1</sub>—II<sub>2</sub>—

B.P. 137° at 15 mm. (1)

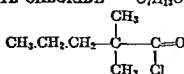
[For prepn. of  $\bar{C}$  from pimelic acid (1:0456) with excess  $\text{SOCl}_2$  (1) (2) see indic. refs.][ $\bar{C}$  with 1 mole MeOH should give 6-carbomethoxyhexanoyl chloride-1, b.p. 135-136° at 17 mm. (3), usually prepd. (3) from methyl hydrogen pimelate +  $\text{SOCl}_2$ .] $\bar{C}$  +  $\text{AlCl}_3$  +  $\text{C}_6\text{H}_6$  yields (2) 1,5-diphenylpentanedione-1,5. $\bar{C}$  on hydrolysis yields pimelic acid (1:0456) (for the dianilide, di-*p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see 1:0456).3:9450 (1) Blaise, Koehler, *Bull. soc. chim.* (4) 5: 687 (1909). (2) Skraup, Guggenheimer, *Ber.* 58, 2498 (1925). (3) Morgan, Walton, *J. Chem. Soc.* 1935, 291.3:9452 *d,l*- $\alpha$ -METHYL-*n*-CAPROYL CHLORIDE

Beil. II - 342

(n-Butyl-methyl-acetyl chloride)

II<sub>1</sub>—II<sub>2</sub>-(296)Physical constants for  $\bar{C}$  appear to be as yet unrecorded. [The dextrorotatory stereoisomer of  $\bar{C}$ , b.p. 45-48° at 9 mm. (1) (amide, m.p. 66° (1)), has been obt'd. from the dextrorotatory acid with  $\text{SOCl}_2$  (1).][For prepn. of  $\bar{C}$  from *n*-butyl-methyl-acetic acid (1:1134) with  $\text{PCl}_5$  (2) or with  $\text{SOCl}_2$  (3) see indic. refs.] $\bar{C}$  on hydrolysis yields 2-methylhexanoic acid-1 (*n*-butyl-methyl-acetic acid) (1:1134) (for the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see 1:1134).3:9452 (1) Levene, Mikesa, *J. Biol. Chem.* 84, 581-582 (1929). (2) Rasetti, *Bull. soc. chim.* (3) 33, 690 (1905). (3) Reichstein, Trivelli, *Helv. Chim. Acta* 15, 258-259 (1932).3:9456  $\alpha,\alpha$ -DIMETHYL-*n*-VALERYL CHLORIDE

Beil. S.N. 162

(Dimethyl-*n*-propyl-acetyl chloride)

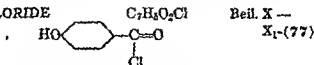
B.P. 45° at 10 mm. (1)

[For prepn. of  $\bar{C}$  from  $\alpha,\alpha$ -dimethyl-*n*-valeric acid [Beil. II-345] see (1).] $\bar{C}$  on hydrolysis yields  $\alpha,\alpha$ -dimethyl-*n*-valeric acid (see above), b.p. 199-200°, 101-102° at 11 mm. (2), 98-99° at 9 mm. (1).① Dimethyl-*n*-propyl-acet-amide: m.p. 95-96° (1) (2).

from hot aq., m.p. 167° (1);  $\bar{C}$  with -- -- -- -- --  
 XII-502, XII<sub>1</sub>-(269)], ndls. from -- -- -- -- --  
 p-toluidine in CHCl<sub>3</sub> yields (1); -- -- -- -- -- benzo-p-toluidide, ndls. from dil. alc., m.p. 163° (1).

3:9446 (1) Anschütz, Krone, *Ann.* 442, 41-42 (1925). (2) Kopetschni, Karczag, *Ger.* 262,783, July 25, 1913; *Cent.* 1913, II 728. (3) Kopetschni, Karczag, *Ger.* 266,351, Oct. 21, 1913; *Cent.* 1913, II 1715. (4) Klemenc, *Ber.* 49, 1373 (1916). (5) Kupferberg, *J. prakt. Chem.* (2) 18, 445 (1877).

## 3:9447 4-HYDROXYBENZOYL CHLORIDE



The precise physical props of  $\bar{C}$  have never been reported; it appears to be a yellow oil still liquid at -15° (1) which cannot be distilled with decompn. even in high vac. (2);  $\bar{C}$  has odor and lachrymatory character of benzoyl chloride (2)

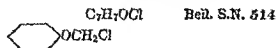
{For prepn. of  $\bar{C}$  from Na or K salt of -- -- -- -- -- benzoic acid (1:0840) with SOCl<sub>2</sub> (1) (4) or with COCl<sub>2</sub> from p-hydroxybenzoic acid (1:0840) with 4 -- -- -- -- -- or SbCl<sub>5</sub> see (5) }

$\bar{C}$  with -- -- -- -- -- yields methyl p-hydroxybenzoate (1:1549), m.p. 131°;  $\bar{C}$  with EtOH yields (2) ethyl p-hydroxybenzoate (1:1534), m.p. 116°, 112.5° (2);  $\bar{C}$  with dry NH<sub>3</sub> gas in CHCl<sub>3</sub> yields p-hydroxybenzamide, ndls. with 1 H<sub>2</sub>O from aq., m.p. 162° (2);  $\bar{C}$  with aniline in CHCl<sub>3</sub> yields p-hydroxybenzanilide [Beil. XII-502, XII<sub>1</sub>-(269)], lfts. from hot aq., m.p. 196-197° (2);  $\bar{C}$  with p-toluidine in CHCl<sub>3</sub> yields p-hydroxybenzo-p-toluidide, ndls. from alc., m.p. 203-204° (2).

3:9447 (1) Kopetschni, Karczag, *Ger.* 262,883, July 25, 1913, *Cent.* 1913, II 728. (2) Anschütz, Zerbe, *Ann.* 442, 38 (1925). (3) Kopetschni, Karczag, *Ger.* 266,351, Oct. 21, 1913, *Cent.* 1913, II 1715. (4) Kopetschni, Karczag, *Ber.* 47, 237 (1914). (5) Kissling (to I.G.), *Ger.* 701,953, Jan. 2, 1910; *C.A.* 36, 99 (1942).

## 3:9448 PHENOXYMETHYL CHLORIDE

(Chloromethyl phenyl ether;  
 α-chloroanisole;  
 ω-chloroanisole)



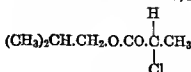
Authentic physical constants for this compound are unreported.

{For attempts to prepare  $\bar{C}$  from methylene (di)chloride (3:5020) (1) or from chloromethyl acetate (3:3356) (2) by reaction with sodium phenolate, from formaldehyde diphenylacetal (diphenoxymethane) [Beil. VI-156] by partial cleavage to phenoxymethyl alcohol followed by conversion to  $\bar{C}$  (1), or from anisole (1:7445) by chlorination (3) see indic. refs.]

{For claim on use of  $\bar{C}$  in refining of mineral oils see (4).}

3:9448 (1) Bentley, Haworth, Perkin, *J. Chem. Soc.* 69, 166-167 (1896). (2) Kirner, *J. Am. Chem. Soc.* 43, 2747-2748 (1926). (3) Weygand, Vogel, *J. prakt. Chem.* (2) 155, 342-348 (1940). (4) Clarke, Towne (to Texas Co.), U.S. 2,075,269, March 30, 1937; *Cent.* 1937, II 330; *C.A.* 31, 3686 (1937).

3:9470 ISOBUTYL *d,l*- $\alpha$ -CHLOROPROPIONATE  $C_7H_{13}O_2Cl$  Beil. S.N. 162



B.P. —

$$D_4^{20} = 1.0175 \text{ (1)} \quad n_D^{20} = 1.4230 \text{ (1)}$$

3:9470 (1) Schjanberg, *Z. physik. Chem.* A-172, 230 (1935).

3:9474 *n*-BUTYL  $\beta$ -CHLOROPROPIONATE  $C_7H_{13}O_2Cl$  Beil. II —  
 $n\text{-C}_4\text{H}_9\text{O.CO.CH}_2\text{CH}_2\text{Cl}$  II<sub>1</sub>—  
 II<sub>2</sub>-(227)

B.P. 104° at 22 mm. (1)

$$D_4^{20} = 1.0394 \text{ (2)} \quad n_D^{20} = 1.4321 \text{ (2)}$$

97° at 15 mm. (1)

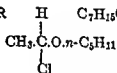
$$D_4^{15} = 1.0708 \text{ (1)} \quad n_D^{15} = 1.4385 \text{ (1)}$$

[For prepn. from *n*-butyl alc. (1:6180) +  $\beta$ -chloropropionic ac. (3:0460) see (1).]

$\bar{C}$  htd. at 200° with diethylaniline loses HCl and gives (90-100% yield (1)) in distillate *n*-butyl acrylate, b.p. 138-140° at 756 mm. (1).

3:9474 (1) Moureu, Murat, Tampier, *Ann. chim.* (9) 15, 246, 251 (1921). (2) Schjanberg, *Z. physik. Chem.* A-172, 231 (1935).

3:9480 *n*-AMYL  $\alpha$ -CHLOROETHYL ETHER  $C_7H_{15}OCl$  Beil. S.N. 78  
 ( $\alpha$ -Chloroethyl *n*-amyl ether)



B.P. 63.3-66.3° cor. at 8 mm. (1)

$$D_4^{20} = 0.9200 \text{ (1)} \quad n_D^{20} = 1.4218 \text{ (1)}$$

[For prepn. (99% yield (1)) from paraldehyde (1:0170) + *n*-amyl alc. (1:6205) + dry HCl see (1).]

$\bar{C}$  on stdg. polymerizes to dark tarry residue (1).

$\bar{C}$  on shaking with aq. yields acetaldehyde (1:0100), *n*-amyl alc. (1:6205), + HCl.

3:9480 (1) Henze, Murchison, *J. Am. Chem. Soc.* 53, 4077-4079 (1931).

3:9400  $\beta$ -CHLOROPROPIONALDEHYDE DIETHYLACETAL Beil. I - 632  
 $ClCH_2.CH_2.CH(OC_2H_5)_2$   $C_7H_{13}O_2Cl$  I<sub>1</sub>-(335)  
 I<sub>2</sub>-(690)

B.P. 84° at 25 mm. (1)

$$D_4^{22.3} = 0.9845 \text{ (2)} \quad n_D^{22.3} = 1.4203 \text{ (2)}$$

74° at 20 mm. (2) (10)

$$D_4^{18.7} = 0.9051 \text{ (2)} \quad n_D^{18.7} = 1.4206 \text{ (2)}$$

56-66° at 8 mm. (3)

47-50° at 3-4 mm. (4)

Oil, insol. in aq. but sol. in org. solvents. —  $\bar{C}$  may be preserved only if completely free from acid (11) and should be kept over moist  $K_2CO_3$  (3). —  $\bar{C}$  on htg. dec. at abt. 145° yielding (1) HCl and acrolein (1:0115).

[For prepn. from acrolein (1:0115) in abs. alc. at 0° with HCl gas (34% yield (5)) (6) (7) (11) (12) in the presence of  $CaCl_2$  (90% yield (3), 56% yield (8)) see indic. refs.; for prepn. from  $\alpha,\gamma$ -dichloro-*n*-propyl ethyl ether (9) by reactn. in the cold with EtOH (83% yield (9)) (1) or with NaOEt (1) see indic. refs.]

3:9456 (1) Locquin, Leers, *Compt. rend.* 178, 2097 (1924). (2) Haller, Bauer, *Compt. rend.* 148, 129 (1909).

3:9458  $\alpha,\beta$ -DIMETHYL-*n*-VALERYL CHLORIDE  $C_7H_{13}OCl$  Beil. S.N. 162  
(*sec.*-Butyl-methyl-acetyl chloride)  

$$\begin{array}{ccccccc} & & & & C_7H_{13}OCl & & \\ & & & & | & & \\ CH_3 & CH_2 & -CH- & CH- & C=O & & \\ & & | & | & | & & \\ & & CH_3 & CH_3 & Cl & & \end{array}$$

B.P. 110-113° at 193 mm. (1)

[For prepn. of  $\tilde{C}$  from  $\alpha,\beta$ -dimethyl-*n*-valeric acid (1) see (1).]

$\tilde{C}$  on hydrolysis yields  $\alpha,\beta$ -dimethyl-*n*-valeric acid, b.p. 210.5-210.8° at 750 mm. (1),  $D_{18}^{20} = 0.9316$  (methyl ester, b.p. 155-158° at 743 mm. (1)).

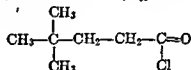
①  $\alpha,\beta$ -Dimethyl-*n*-valeramide: m.p. 101-103° (1)

②  $\alpha,\beta$ -Dimethyl-*n*-valeranilide: m.p. 71-72° (1)

③  $\alpha,\beta$ -Dimethyl-*n*-valero-*p*-bromoanilide: m.p. 115-117° (1).

3:9458 (1) Chichibabin, Katznelson, *Bull. acad. sci. U.R.S.S., Classe sci. math. nat.* 1933, 267-271; *Cent.* 1933, II 3409; *C.A.* 27, 3698 (1933).

3:9460  $\gamma,\gamma$ -DIMETHYL-*n*-VALERYL CHLORIDE  $C_7H_{13}OCl$  Beil. S.N. 162  
(Neopentylacetyl chloride)



B.P. 94° at 100 mm. (1)

$n_D^{20} = 1.4294$  (1)

[For prepn. of  $\tilde{C}$  from neopentylacetic acid (1) with  $SOCl_2$  see (1).]

[ $\tilde{C}$  with a large excess of *ter*-BuMgCl (4 moles) gives (1) 67% yield 2,2,6,6-tetramethylheptanol-3, m.p. 58-59° (1) (3,5-dinitrobenzoate, m.p. 99.5° (1); *N*-( $\alpha$ -naphthyl)carbamate, m.p. 92° (1), and 13.5% 2,2-dimethylpentanol-5, b.p. 160° at 728 mm. (1), 158° at 737 mm. (2), 96° at 62 mm. (2),  $D_4^{20} = 0.815$  (2),  $n_D^{20} = 1.4202$  (2) (*N*-( $\alpha$ -naphthyl)carbamate, m.p. 80.5-81° (2)).]

$\tilde{C}$  on hydrolysis presumably yields neopentylacetic acid, b.p. 159° at 150 mm. (1),  $n_D^{20} = 1.4215$  (1).

3:9460 (1) Whitmore, Whitaker, Mosher, Breivik, Wheeler, Miner, Sutherland, Wagner, Clapper, Lewis, Lux, Popkin, *J. Am. Chem. Soc.* 63, 647 (1941). (2) Whitmore, Homeyer, *J. Am. Chem. Soc.* 55, 4558 (1933).

3:9462  $\alpha$ -ETHYL- $\beta$ -METHYL-*n*-BUTYRYL CHLORIDE  $C_7H_{13}OCl$  Beil. S.N. 162  
( $\alpha$ -Ethyl-isovaleryl chloride;  
ethyl-isopropyl-acetyl chloride)  

$$\begin{array}{ccccccc} & & & & C_7H_{13}OCl & & \\ & & & & | & & \\ CH_3 & -CH- & CH- & C=O & & & \\ & | & | & | & & & \\ & CH_3 & C_2H_5 & Cl & & & \end{array}$$

B.P. 63-65° at 12 mm. (1)

[For prepn. of  $\tilde{C}$  from ethyl-isopropyl-acetic acid [Beil. II-345, II-1(147)] see (1).]

$\tilde{C}$  on hydrolysis yields  $\alpha$ -ethyl-isovaleric acid (see above), b.p. 202-203° (1), 202-204° (2).

① Ethyl-isopropyl-acet-amide: ndls. from aq., m.p. 136° cor. (3), 134-135.5° (2), 134° (2). [From  $\tilde{C}$  +  $NH_3$  at 180° (2).]

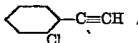
② Ethyl-isopropyl-acet-anilide: ndls. from lgr., m.p. 114-115° (1).

③ Ethyl-isopropyl-acet-*p*-toluidide: ndls. from lt. pet. m.p. 122.5-123° (2).

3:9462 (1) Nenitzescu, Chicos, *Ber.* 68, 1587 (1935). (2) Crossley, Le Sueur, *J. Chem. Soc.* 77, 94 (1900). (3) Fischer, Robde, Brauns, *Ann.* 402, 375-376 (1914).



(2) Nef, *Ann.* **308**, 316-323 (1898). (3) Cleve, 939). (4) Ott, Bossaller, *Ber.* **76**, 89-90 (1943); *Compt. rend.* **190**, 753-755 (1930). (6) Truchet, *Ann. chim.* (10) **16**, 320-327, 335-337, 340-358 (1931). (7) Murray, *J. Am. Chem. Soc.* **60**, 2663 (1938). (8) Wilson, Wenzke, *J. Am. Chem. Soc.* **56**, 2026 (1934). (9) Gilman, Fothergill, *J. Am. Chem. Soc.* **51**, 3506 (1929).

3:9497 *o*-CHLOROPHENYLACETYLENEC<sub>8</sub>H<sub>5</sub>Cl Beil. S.N. 474

B.P. 71° at 18 mm. (1) (2)

 $D_D^{25} = 1.1249$  (2)  $n_D^{25} = 1.5690$  (2)

[For prepn. of  $\bar{C}$  from *o*-chlorophenylpropionic acid (3:3956) by elimination of CO<sub>2</sub> with NaHCO<sub>3</sub> + CuCl<sub>2</sub> (66% yield (1)) or Cu(OAc)<sub>2</sub> (yield not stated (2)) see indic. refs.]

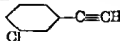
[For study of dipole moment see (3).]

$\bar{C}$  with PCl<sub>5</sub> (3 wt. pts.) in C<sub>6</sub>H<sub>6</sub> stood 24 hrs. then poured into aq. gives (54% yield (1))  $\alpha$ -chloro- $\alpha$ -(*o*-chlorophenyl)ethylene- $\beta$ -phosphinic acid (C<sub>8</sub>H<sub>7</sub>O<sub>3</sub>Cl<sub>2</sub>P), lfts. from dil. HCl, m.p. 187° (1). — [This prod. with 5% aq. KOH boiled for 6 hrs. loses HCl, giving (1) upon acidification *o*-chlorophenylacetylenephosphinic acid (C<sub>8</sub>H<sub>5</sub>O<sub>3</sub>ClP), lfts. from C<sub>6</sub>H<sub>6</sub>/AcOH, m.p. 134° (1).]

[ $\bar{C}$  with I<sub>2</sub> in liq. NH<sub>3</sub> at -34° readily gives (95% yield (4)) *o*-chlorophenyl-iodo-acetylene, cryst. from MeOH, m.p. 37.7-38.0° (4).]

Ⓒ Di-(*o*-chlorophenylethynyl)mercury: m.p. 213-214° (2). [From  $\bar{C}$  in alc. with alk. K<sub>2</sub>HgI<sub>4</sub> according to (5); note, however, that m.p. of this prod. is only slightly lower than that (221-222°) of the corresp. prod. from *p*-chlorophenylacetylene (3:0590).]

3:9497 (1) Bergmann, Bondi, *Ber.* **66**, 282-283 (1933). (2) Otto, *J. Am. Chem. Soc.* **56**, 1393-1394 (1934). (3) Otto, Wenzke, *J. Am. Chem. Soc.* **56**, 1314-1315 (1934). (4) Vaughn, Nieuwland, *J. Am. Chem. Soc.* **56**, 1207-1209 (1934). (5) Johnson, McEwen, *J. Am. Chem. Soc.* **48**, 471 (1926).

3:9500 *m*-CHLOROPHENYLACETYLENEC<sub>8</sub>H<sub>5</sub>Cl Beil. S.N. 474

B.P. 64-65° at 12 mm. (1)

[See also *o*-chlorophenylacetylene (3:9497).]

[For prepn. of  $\bar{C}$  from *m*-chlorophenylpropionic acid (3:4102) by elimination of CO<sub>2</sub> with Cu(OAc)<sub>2</sub> (yield not stated) see (1); for formn. of  $\bar{C}$  from *m*-chlorocumene by pyrolysis see (5).]

[For study of dipole moment see (2).]

[ $\bar{C}$  with I<sub>2</sub> in liq. NH<sub>3</sub> at -34° readily gives (91% yield (3)) *m*-chlorophenyl-iodo-acetylene, m.p. 11.1°,  $D_D^{25} = 1.818$ ,  $n_D^{25} = 1.6638$  (3).]

Ⓒ Di-(*m*-chlorophenylethynyl)mercury: m.p. 133-139° (2), 138.0-138.5° (3). [From  $\bar{C}$  in alc. with alk. K<sub>2</sub>HgI<sub>4</sub> according to (4).]

3:9500 (1) Otto, *J. Am. Chem. Soc.* **56**, 1393-1394 (1934). (2) Otto, Wenzke, *J. Am. Chem. Soc.* **56**, 1314-1315 (1934). (3) Vaughn, Nieuwland, *J. Am. Chem. Soc.* **56**, 1207-1209 (1934). (4) Johnson, McEwen, *J. Am. Chem. Soc.* **48**, 471 (1926). (5) Dreisbach (to Dow Chem. Co.), U.S. 2,110,830, March 8, 1938; *Cent.* 1938, I 4110; *C.A.* **32**, 3426 (1938).

$\bar{C}$  readily hydrolyzes in the presence of dil. acid yielding  $\beta$ -chloropropionaldehyde (3:5576) q.v. and EtOH (1:6130) q.v.

$\bar{C}$  on refluxing with 2 moles aq. soon undergoes spontaneous reactn., the initial two layers becoming miscible, and after rapid cooling and shaking with conc.  $\text{KHSO}_3$  or  $\text{NaHSO}_3$  soln. gives (2) upon addn. of alcohol a ppt. of the corresp. bisulfite cpd. of  $\beta$ -chloropropionaldehyde (3:5576).

[ $\bar{C}$  shaken with a large excess (6 moles) of powdered KOH, then htd at  $210-220^\circ$ , gives (yields: 75% (13), 70% (8)) (10) (3) (12) acrolein diethylacetal (1:0169) q.v., b p.  $123^\circ$ . —  $\bar{C}$  on shaking with dil. aq. NaOH at  $115^\circ$  yields (11)  $\beta$ -hydroxypropionaldehyde diethylacetal [Beil. I-820, I<sub>1</sub>-(418)].]

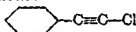
[For reactn. of  $\bar{C}$  with aniline (14) (15), with hydrazine hydrate (16), with alcoholates or phenolates (17), with diethyl sodiomalonate (18), with  $\text{MeNH}_2$  (19), or with sodium methyl mercaptide (20) see indic. refs.]

3:9490 (1) Brabant, *Z. physiol. Chem.* 86, 208-209 (1913). (2) Crawford, Kenyon, *J. Chem. Soc.* 1927, 399. (3) Witzemann, *J. Am. Chem. Soc.* 36, 1909-1912 (1914). (4) Hartung, Adkins, *J. Am. Chem. Soc.* 49, 2521 (1927). (5) Witzemann, Evans, Hass, Schroeder, *Org. Syntheses*, Coll. Vol. 2 (1st ed.), 137-138 (1943). (6) Neuberg, Wendisch, *Biochem. Z.* 166, 480 (1925). (7) Evans, Hass, *J. Am. Chem. Soc.* 48, 2705-2706 (1926). (8) Reeves, *J. Chem. Soc.* 1927, 2481. (9) Duhère, *Bull. soc. chim.* (4) 33, 1651-1652 (1923). (10) Wohl, *Ber.* 31, 1797-1798 (1898).

(11) Wohl, *Emmerich, Ber.* 33, 2761 (1900). (12) Spoehr, Young, *Carnegie Inst. Wash. Yearbook* 23, 175-177 (1925/6). *Expt. Sta. Record*, 57, 817, *C. A.* 22, 2368 (1928). (13) Witzemann, Evans, Hass, Schroeder, *Org. Syntheses*, Coll. Vol. 2 (1st ed.), 17-18 (1943). (14) Barr, *J. Am. Chem. Soc.* 53, 2422-2425 (1930). (15) Rath, *Ber.* 57, 717 (1924). (16) Wohl, *Ber.* 64, 1384 (1931). (17) Schorigin, Korschak, *Ber.* 68, 841-844 (1935). (18) Ellinger, *Ber.* 38, 2886 (1905). (19) Wohl, Johnson, *Ber.* 40, 4714 (1907). (20) Barger, Coyne, *Biochem. J.* 22, 1420 (1928).

### 3:9494 $\alpha$ -CHLORO- $\beta$ -PHENYLACETYLENE

(Chloroethynylbenzene,  
phenylethynyl chloride;  
 $\omega$ -chlorophenylacetylene)



$\text{C}_8\text{H}_5\text{Cl}$

Beil. V-513

V<sub>1</sub>—

V<sub>2</sub>—

B.P. $74^\circ$	at 15 mm. (1)
$74^\circ$	at 14 mm. (2)
$73^\circ$	at 16 mm. (3)
$72^\circ$	at 15 mm. (4)
$71.5-72^\circ$	at 15 mm. (5)
$71^\circ$	at 16 mm. (6)

$$D_{20}^{18} = 1.126 \text{ (5) (6)} \quad n_D^{18} = 1.576 \text{ (5) (6)}$$

$$n_D^{19} = 1.5708 \text{ (6)}$$

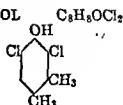
Colorless mobile liq. with strong and characteristic odor. — Polymerizes rapidly on stdg. with sepn. of crystals (never identified) (7).

[For prepn. of  $\bar{C}$  from sodium deriv. of phenylacetylene (1:7425) in dry ether with *p*-toluenesulfonyl chloride (65% yield (6)) (3) (7) or benzenesulfonyl chloride (yield 54% (6)) (8) see indic. refs.; from phenylethynyl  $\text{MgBr}$  in dry ether with benzenesulfonyl chloride (yields: 35% (6), 13.7% (9)) or *p*-toluenesulfonyl chloride (33% yield (6)) see indic. refs.; from dichloroacetylene (3:5010) with  $\text{C}_6\text{H}_5\text{MgX}$  (70% yield) see (4); from sodium or silver salts of phenylacetylene (1:7425) with  $\text{SO}_2\text{Cl}_2$  in dry ether (small yield) see (2); from  $\omega,\omega$ -dichlorostyrene ( $\alpha,\alpha$ -dichloro- $\beta$ -phenylethylene) [Beil. V-477, V<sub>2</sub>-(367)] by elimination of 1 HCl with alc. KOH (1 mole) at  $100^\circ$  for 1 hr. see (2).]

$\bar{C}$  on protracted boilg. with excess alc. KOH followed by acidification yields (2) (6) phenylacetic acid (1:0665).

[For reactn. of  $\bar{C}$  with diethyl sodiomalonate see (2) (6).]

$\bar{C}$  does not react with KI in acetone (7).

3:0925 (1) Szenic, Taggesell, *Ber.* 28, 2665-2672 (1895).3:0935 2,6-DICHLORO-3,4-DIMETHYLPHENOL  
(3,5-Dichloro-*o*-4-xenol)Beil. VI —  
VI—  
VI<sub>2</sub>-(456)

M.P. 52° (1)

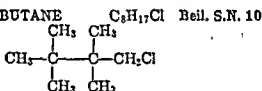
Cryst. from lt. pet. — Volatile with steam.

[For prepn. of  $\bar{C}$  from 6-chloro-2-amino-3,4-dimethylphenol (5-chloro-3-amino-*o*-4-xenol) (1) via diazotization and reaction with  $\text{Cu}_2\text{Cl}_2$  (yield not stated) see (1); from 2,6-dichloro-3,4-dimethylanilino (3,5-dichloro-*o*-4-xyldine) (2) via diazotization and hydrolysis (yield not stated) see (1).]

The nitration of  $\bar{C}$  has not been reported, and the expected 5-nitro-2,6-dichloro-3,4-dimethylphenol is unknown.

— 2,6-Dichloro-3,4-dimethylphenyl acetate: unreported.

⑩ 2,6-Dichloro-3,4-dimethylphenyl benzoate: m.p. 89° (1).

3:0935 (1) Hinkel, Ayling, Bevan, *J. Chem. Soc.* 1928, 2532. (2) Hinkel, Ayling, Bevan, *J. Chem. Soc.* 1928, 1878.3:0945 1-CHLORO-2,2,3,3-TETRAMETHYLBUTANE  
(Chlorohexamethylethane)

Beil. S.N. 10

M.P. 52-53° (1)

B.P. 80-81° at 40 mm. (1)

Soft waxy solid with characteristic alkyl halide odor; on long stdg. the opaque crystn. structure disappears and  $\bar{C}$  becomes transparent (1).

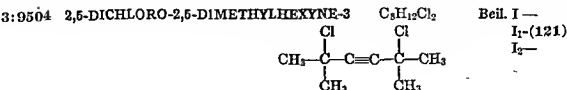
[For prepn. of  $\bar{C}$  from 2,2,3,3-tetramethylbutane (hexamethylethane) (1:7090) with  $\text{Cl}_2$  in  $\text{CCl}_4$  soln. in sunlight (33% yield together with other products) see (1).]

$\bar{C}$  with Mg + trace of  $\text{I}_2$  + a little  $\text{C}_2\text{H}_5\text{Br}$  in dry ether gives in 19 hrs. 70% yield corresp.  $\text{RMgCl}$  (accompanied by 24% 2,2,3,3,6,6,7,7-octamethyloctane, pl. from  $\text{MeOH}$ , m.p. 74.0-74.5°, from coupling of  $\bar{C}$ ) (1).

$\bar{C}$  converted (as above) to  $\text{RMgCl}$ , treated with wet ether, and poured into dil.  $\text{H}_2\text{SO}_4$  gives (1) hexamethylethane (1:7090), m.p. 101-102° (1).

$\bar{C}$  converted to  $\text{RMgCl}$  (as above) and the ether soln. treated at  $-5^\circ$  with  $\text{CO}_2$  gives (59% yield (1)) 3,3,4,4-tetramethylpentanoic acid, cryst. from dil.  $\text{MeOH}$ , m.p. 66-67° (1). [This acid with  $\text{SOCl}_2$  in  $\text{C}_6\text{H}_6$  gives (80% yield (1)) the corresp. acid chloride, b.p. 87-88° at 20 mm.,  $D_4^{20} = 0.9821$ ,  $n_D^{20} = 1.4557$ ; the latter with dry  $\text{NH}_3$  in ether gives (77% yield (1)) the corresp. amide, cryst. from  $\text{CHCl}_3$ , m.p. 137-138° (a second cryst. form from  $\text{MeOH}$  has m.p. 149-150° but after fusion melts 137-138°), or with aniline in ether gives the corresp. anilide, cryst. from pet. eth., m.p. 175-176° (1).]

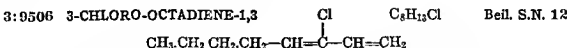
$\bar{C}$  converted to  $\text{RMgCl}$  (as above) and the ether soln. treated at  $-5^\circ$  with dry  $\text{O}_2$  for 4 hrs. gives (53% yield (1)) 2,2,3,3-tetramethylbutanol-1, very volatile solid, m.p. 149-150° [corresp. 3,5-dioitrobenzoate, m.p. 88-90°; *N*-phenylcarbamate, m.p. 65-66° (1)].



B.P. 62–63° at 15 mm. (1) M.P. 29° (1)

[From 2,5-dimethylhexyn-3-diol-2,5 [Beil. I-591, I<sub>1</sub>-(263)] with HCl at 0° see (1).]

3:9504 (1) Dupont, *Compt. rend* 152, 198 (1911).



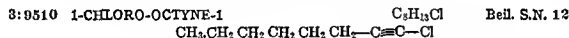
B.P. 64–65° at 18 mm. (1) (3)  $D_4^{20} = 0.9366$  (1)  $n_D^{20} = 1.4794$  (1)

[For prepn. of  $\bar{C}$  from 1-*n*-butyl-2-vinylacetylene (2) by shaking with conc. HCl contg.  $\text{Cu}_2\text{Cl}_2 + \text{NH}_4\text{Cl}$  see (1).]

$\bar{C}$  htd.  $\frac{1}{2}$  pt. naphthoquinone-1,4 (1:9040) at 100° for 2 hrs., prod. suspended in alc. NaOH and aerated, yields (1) 1-*n*-butyl-2-chloroanthraquinone, yel. ndls. from MeOH, mp. 129–130° (1).

[For polymerization of  $\bar{C}$  see (1) (3).]

3:9506 (1) Jacobson, Carothers, *J. Am. Chem. Soc.* 55, 1624–1627 (1933). (2) Jacobson, Carothers, *J. Am. Chem. Soc.* 55, 1622–1624 (1933). (3) Carothers, Coffman, U.S. 1,950,441, March 13, 1934; *Cent.* 1934, 11 1037, *C.A.* 28, 3270 (1934).



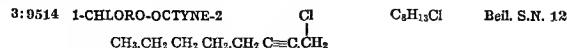
B.P. 61–62° at 17 mm. (1)  $D_4^{20} = 0.912$  (1)  $n_D^{20} = 1.445$  (1)

[For prepn. of  $\bar{C}$  from octyne-1 (*n*-hexylacetylene) (1.8105) via conversion with  $\text{NaNH}_2$  to  $\text{C}_6\text{H}_{13}.\text{C}\equiv\text{C}-\text{Na}$  and reaction in ether with hezenesulfonyl chloride (65% yield (1)) see (1) ]

[Refractive indices via Pulfrich instrument:  $n_D^{12.7} = 1.4447$ ,  $n_D^{12.7} = 1.4472$ ,  $n_F^{12.7} = 1.4536$ ,  $n_G^{12.7} = 1.4589$  (1) ]

$\bar{C}$  on refluxing for 12 hrs. with alc. KOH gives (79% yield (1)) *n*-caprylic acid (1:1145).

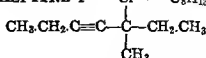
3:9510 (1) Truchet, *Ann. chim.* (10) 16, 334, 337, 351 (1931).



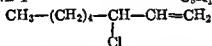
B.P. 80.5–81° at 15 mm. (1)

[For prepn. of  $\bar{C}$  from octyn-2-ol-1 [Beil I-456, I<sub>1</sub>-(236), I<sub>2</sub>-(506)] with  $\text{PCl}_3$  see (1).]

3:9514 (1) Toussaint, Wenzke, *J. Am. Chem. Soc.* 57, 668–669 (1935).

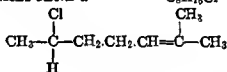
3:9516 3-CHLORO-3-METHYLHEPTYNE-4 · Cl · C<sub>8</sub>H<sub>13</sub>Cl · Beil. S.N. 12

B.P. 55° at 130 mm. (1)

 $D_4^{20} = 0.9163$  (1)  $n_D^{20} = 1.4330$  (1)[For prepn. of  $\bar{C}$  from 3-methylheptyn-4-ol-3 (1) by saturation with HCl gas (60% yield) see (1).][ $\bar{C}$  with MeMgBr gives (66% yield) 3,3-dimethylheptyne-4, b.p. 69° at 100 mm.,  $D_4^{20} = 0.7610$ ,  $n_D^{20} = 1.4360$  (1);  $\bar{C}$  with EtMgBr gives (61% yield) 3-ethyl-3-methyl-heptyne-4, b.p. 88° at 100 mm.,  $D_4^{20} = 0.7714$ ,  $n_D^{20} = 1.4386$  (1).]3:9516 (1) Campbell, Eby, *J. Am. Chem. Soc.* 62, 1799-1800 (1940).3:9518 *d,l*-3-CHLORO-OCTENE-1 C<sub>8</sub>H<sub>15</sub>Cl Beil. S.N. 11

No record of this compound can be found in the literature.

[Note, however, that the levorotatory enantiomorph has been reported (1).]

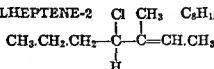
3:9518 (1) Levene, Rothen, *J. Chem. Phys.* 5, 982 (1937).3:9520 6-CHLORO-2-METHYLHEPTENE-2 C<sub>8</sub>H<sub>15</sub>Cl Beil. I —  
I<sub>1</sub>—  
I<sub>2</sub>-(200)

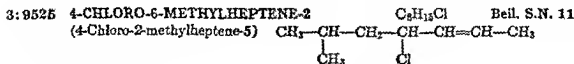
B.P. 60-61° at 15 mm. (1)

 $D_4^{18} = 0.8931$  (1)  $n_D^{18} = 1.4458$  (1)

59-61° at 15 mm. (2)

Colorless mobile liq., insof. aq., sol. in usual org. solvents.

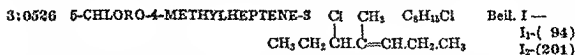
[For prepn. from 2-methylhepten-2-ol-6 [Beil. I-448, I<sub>1</sub>-(230), I<sub>2</sub>-(490)] with SOCl<sub>2</sub> + pyridine (39% yield (1)) see (1) (2).] $\bar{C}$  could not be induced to yield an R.MgCl cpd. (2). $\bar{C}$  in AcOH treated with O<sub>3</sub> and the soln. subsequently shaken with Zn dust gives (61% yield (1))  $\gamma$ -chloro-*n*-valeraldehyde, b.p. 70-71° at 16 mm. (1).3:9520 (1) Helferich, Dommer, *Ber.* 53, 2008-2009 (1920). (2) Doeuvre, *Bull. soc. chim.* (4) 45, 359-360 (1929).3:9524 *d,l*-4-CHLORO-3-METHYLHEPTENE-2 Cl CH<sub>3</sub> C<sub>8</sub>H<sub>15</sub>Cl Beil. I —  
I<sub>1</sub>-(94)  
I<sub>2</sub>—[For prepn. of  $\bar{C}$  from 3-methylhepten-2-ol-4 (1) with 6 N HCl see (1).]3:9524 (1) Abelmann, *Ber.* 43, 1581 (1910).



B.P. 57° at 13 mm. (1)

[For prepn. of  $\tilde{\text{C}}$  from 6-methylhepten-2-ol-4 with HCl see (1).]

3:9525 (1) Knorr (to I.G.), Ger. 553,279, June 24, 1932; *Cent.* 1932, II 2370; *C.A.* 26, 4611 (1932).



B.P. 75-78° at 53 mm. (1)

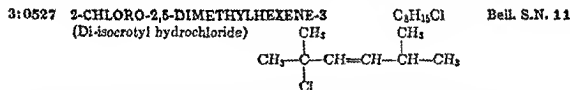
Two geom. stereoisomers of  $\tilde{\text{C}}$  are possible, but only this one is as yet recorded.

[For prepn. of  $\tilde{\text{C}}$  from 4-methylhepten-3-ol-5 (Beil. I<sub>1</sub>-(201), I<sub>2</sub>-(491)] by distn. with conc. HCl (1) (3) or by saturation with dry HCl gas at 0° (2) see indic. refs.]

$\tilde{\text{C}}$  is very reactive toward aq; at 15°  $\tilde{\text{C}}$  is 93% hydrolyzed in 48 hrs., at 45-50° 90% hydrolyzed in 75 min (2)

$\tilde{\text{C}}$  on oxidn. with Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>SO<sub>4</sub> at 45-50° yields (2) 4-methylhepten-3-one-5 [Beil. I<sub>2</sub>-(799)], b.p. 170-172° at 735 mm, 96-98° at 70 mm,  $D_4^{15} = 0.8773$ ,  $n_D^{15} = 1.4510$  (2,4-dinitrophenylhydrazone, m.p. 147°, semicarbazone, m.p. 167° (2)).

3:9526 (1) Bjelouss, *Ber.* 43, 2331 (1910). (2) Courtot, Pierron, *Bull. soc. chim.* (4) 45, 292 (1929). (3) Knorr (to I.G.), Ger. 553,279, June 24, 1932, *Cent.* 1932, II 2370.

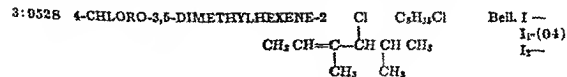


$\tilde{\text{C}}$  has never been reported in pure form; note that, in addition to the possibility of existence of two geometrical stereoisomers,  $\tilde{\text{C}}$  by virtue of allylic rearrangement can yield 4-chloro-2,5-dimethylhexene-2 (3:9529) q.v.

[For prepn. of  $\tilde{\text{C}}$  (as a mixt. with some or all of these other compds) from 2,5-dimethylhexadiene-2,4 ("di-isocrotyl") (Beil. I-259, I<sub>1</sub>-(122), I<sub>2</sub>-(237)] by addn. of dry HCl gas see (1); note that the reaction prod. has b.p. 45-60° at 15 mm.,  $n_D^{20} = 1.45$  to 1.46, and although stable in the cold decomposes on attempts to effect fractional distn.]

$\tilde{\text{C}}$  with MeMgCl yields (1) mainly 2,4,5-trimethylhexene-2 (Beil. I<sub>1</sub>-(95)), b.p. 128.4° at 760 mm. (1),  $D_4^{20} = 0.7403$  (1),  $n_D^{20} = 1.4268$  (1), accompanied by some 2,2,5-trimethylhexene-3, b.p. 114° at 760 mm. (1),  $n_D^{20} = 1.416$  (1) |

3:9527 (1) Henne, Chanan, Turk, *J. Am. Chem. Soc.* 53, 3474-3476 (1931).



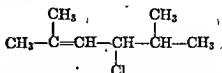
B.P. 58-60° at 21 mm. (1)

[For prepn. of  $\bar{C}$  from 2,4-dimethylhexen-4-ol-3 (1) with 6 N HCl (80% yield) see (1).]

3:9528 (1) Abelmann, *Ber.* 43, 1581-1582 (1910).

3:9529 4-CHLORO-2,5-DIMETHYLHEXENE-2

$C_8H_{15}Cl$  Beil. S.N. 11

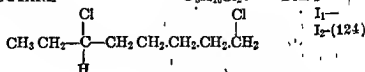


$\bar{C}$ , the allylic rearr. prod. of 2-chloro-2,5-dimethylhexene-3 (3:9527) q.v., has never been reported in pure form (1).

3:9529 (1) Henne, Chanan, Turk, *J. Am. Chem. Soc.* 63, 3474-3476 (1941).

3:9530 *d,l*-1,5-DICHLORO-OCTANE

$C_8H_{16}Cl_2$  Beil. I—



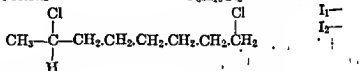
B.P. 105-107° at 16 mm. (1)

[For prepn. of  $\bar{C}$  from *N*-benzoyl-2-*n*-propylpiperidine (*N*-benzoylconiine) [Beil. XX-116] by conversion with  $\text{PCl}_5$  to the amide-chloride  $C_8H_{16}N.C(Cl)_2.C_6H_5$  followed by rapid distn. of the latter see (1).] [This prod. was originally (1) thought to be 1,5-dichlorooctane [Beil. I-160] but is now regarded (2) as  $\bar{C}$ .]

3:9530 (1) von Braun, Schmitz, *Ber.* 39, 4366 (1906). (2) von Braun, Pohl, *Ber.* 57, 482-483 (1924).

3:9532 *d,l*-1,7-DICHLORO-OCTANE

$C_8H_{16}Cl_2$  Beil. I-160



B.P. 132-138° at 20-25 mm. (1)

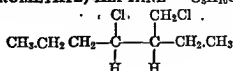
[For prepn. of  $\bar{C}$  from octamethylenediamine [Beil. IV-271] with  $\text{NOCl}$  see (1). The prod. is admittedly impure and contains also 8-chlorooctene-2 and 1,8-dichlorooctane (3:8805).]

$\bar{C}$  on htg. with sodium phenolate yields (1) 1,7-diphenyloctane [Beil. VI-148], b.p. 240-250° at 20-25 mm., not volatile with steam.

3:9532 (1) Ssolonina, *J. Russ. Phys.-Chem. Soc.* 39, 620-621 (1898); *Cent.* 1898, I 26.

3:9534 4-CHLORO-3-(CHLOROMETHYL)-HEPTANE

$C_8H_{15}Cl_2$  Beil. S.N. 10



B.P. 50° at 0.2 mm. (1)

[For prepn. of  $\bar{C}$  from 2-ethylhexanediol-1,2 with conc. HCl at 120° see (1).]

3:9534 (1) von Braun, Manz, *Ber.* 67, 1704-1705 (1934).

3:9536 3,3-DICHLORO-2,2,4-TRIMETHYLPENTANE  $C_8H_{16}Cl_2$  Beil. I —  
(Pentamethylacetone dichloride)  

$$\begin{array}{c} CH_3 \quad Cl \quad CH_3 \\ | \quad | \quad | \\ CH_3 - C - C - C - CH_3 \\ | \quad | \quad | \\ H \quad Cl \quad CH_3 \end{array}$$

B.P. 122-125° at 19 mm. (1)

[For prepn. of  $\bar{C}$  from 2,2,4-trimethylpentanone-3 (pentamethylacetone) [Beil. I-708, I<sub>1</sub>-(364), I<sub>2</sub>-(760)] with  $PCl_5$  in s.t. for 60 hrs. at 140° (1) (together with other products) see (1).]

3:9536 (1) Favorskii, Fritzman, *J. Russ. Phys.-Chem. Soc.* 44, 1353 (1912); *Cent.* 1913, I 1007; *C.A.* 7, 985 (1913); *J. prakt. Chem.* (2) 88, 654 (1913).

3:9538 *d,l*-4-CHLORO-OCTANE  $C_8H_{17}Cl$  Beil. S.N. 10  
(*n*-Butyl-*n*-propyl-carbinyl chloride)  

$$\begin{array}{c} Cl \\ | \\ CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 - C - CH_2 \cdot CH_2 \cdot CH_3 \\ | \\ H \end{array}$$

$\bar{C}$  as such is as yet unreported; however, the dextrorotatory isomer of  $\bar{C}$  has been obtd. (1) from the metalthesis of levorotatory 4-iodooctane with LiCl in MeOH; b.p. 92° at 50 mm.

3:9539 (1) Levene, Rothen, Kuna, *J. Biol. Chem.* 120, 786 (1937).

3:9540 *d,l*-6-CHLORO-2-METHYLHEPTANE  $C_8H_{17}Cl$  Beil. S.N. 10  
(Isohexyl-methyl-carbinyl chloride)  

$$\begin{array}{c} CH_3 \quad Cl \\ | \quad | \\ CH_3 - C - CH_2 \cdot CH_2 \cdot CH_2 - C - CH_3 \\ | \quad | \\ H \quad H \end{array}$$

B.P. 74-75° at 35 mm. (1)

$n_D^{15} = 1.4260$  (1)

[For prepn. of  $\bar{C}$  from 2-methylheptanol-6 [Beil. I-421, I<sub>1</sub>-(209), I<sub>2</sub>-(453)] with  $SOCl_2$  in cold  $CHCl_3$  + dimethylaniline, then refluxed 2 hrs., see (1).]

$\bar{C}$  with activated Mg in dry ether gives with difficulty not over 41% of  $RMgCl$  (by carbocation and titration of the resultant acid (1)).

3:9540 (1) Peak, Robinson, *J. Chem. Soc.* 1937, 1589-1590.

3:9544 3-CHLORO-3-METHYLHEPTANE  $C_8H_{17}Cl$  Beil. S.N. 10  
(*n*-Butyl-ethyl-methyl-carbinyl chloride)  

$$\begin{array}{c} Cl \\ | \\ CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 - C - CH_2 \cdot CH_3 \\ | \\ CH_3 \end{array}$$

B.P. 64-65° at 27 mm. (1)

$D_4^{25} = 0.8720$  (2)  $n_D^{25} = 1.4293$  (3)

55° at 15 mm. (2)

$D_4^{20} = 0.8764$  (2)  $n_D^{20} = 1.4317$  (3)

1.4314 (1)

1.4205 (2)



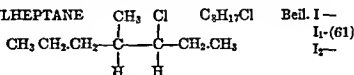
[For prepn. of  $\bar{C}$  from 3-methylheptanol-3 (*n*-butyl-ethyl-methylcarbinol) (Beil. I-421, I<sub>2</sub>-453)] (1) (2) with dry HCl gas at  $-10^\circ$  (2) or at  $10-15^\circ$  (92% yield (1)) see indic. refs.]

$\bar{C}$  with Mg in dry ether as specified (1) gives 70% yield corresp. RMgCl.

$\bar{C}$  converted as above to RMgCl, treated with formaldehyde gas, gives (31% yield (1)) 2-ethyl-2-methylhexanol-1, b.p.  $85.5-86^\circ$  at 11 mm.,  $n_D^{20} = 1.4401$  (1).

3:9544 (1) Whitmore, Badertscher, *J. Am. Chem. Soc.* 55, 1560-1562, 1565 (1933). (2) Whitmore, Woodburn, *J. Am. Chem. Soc.* 55, 361-365 (1933). (3) Smart, Quayle, *J. Am. Chem. Soc.* 67, 21 (1945).

### 3:9548 3-CHLORO-4-METHYLHEPTANE



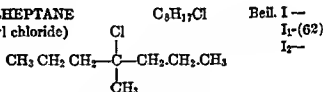
B.P.  $83-86^\circ$  at 79 mm. (1)

[For prepn. of  $\bar{C}$  from 4-methylheptanol-3 with  $\text{PCl}_5$  see (1).]

3:9548 (1) Bijelouss, *Ber.* 45, 628 (1912).

### 3:9550 *d,l*-4-CHLORO-4-METHYLHEPTANE

(Methyl-di-*n*-propyl-carbinyl chloride)



B.P.  $50-51^\circ$  at 12 mm. (1) (3)

$D_4^{20} = 0.8690$  (1)  $n_D^{15} = 1.43098$  (1)

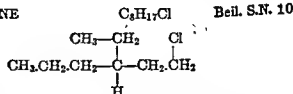
[For prepn. of  $\bar{C}$  from 4-methylheptanol-4 (methyl-di-*n*-propyl-carbinol (1)) by saturation with HCl gas see (1).]

[For data on density of  $\bar{C}$  at  $15^\circ$ ,  $25^\circ$ ,  $50^\circ$ , and  $65^\circ$  and value of parachor at  $0^\circ$ ,  $25^\circ$ ,  $50^\circ$ , and  $75^\circ$  see (2).]

[ $\bar{C}$  with  $\text{C}_6\text{H}_6 + \text{AlCl}_3$  gives (64% yield (1)) 4-methyl-4-phenyl-heptane, h.p.  $120-121^\circ$  at 12 mm.,  $D_4^{20} = 0.8708$ ,  $n_D^{15} = 1.49326$  (1); for behavior with naphthalene +  $\text{AlCl}_3$  in  $\text{CS}_2$  see (3).]

3:9550 (1) Halse, *J. prakt. Chem.* (2) 89, 453-454 (1914). (2) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* 61, 3108 (1939). (3) Petrov, Kurbskii, *J. Gen. Chem. (U.S.S.R.)* 14, 492-494 (1944); *C.A.* 39, 4600 (1945).

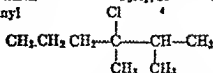
### 3:9552 *d,l*-1-CHLORO-3-ETHYLHEXANE



$\bar{C}$  as such is as yet unreported; however, the dextrorotatory isomer of  $\bar{C}$  has been prepared from dextrorotatory 3-ethylhexanol-1 (1) with  $\text{SOCl}_2$ ; b.p.  $85^\circ$  at 40 mm.,  $D_4^{27} = 0.879$ ,  $n_D^{25} = 1.4335$  (1).

3:9552 (1) Levene, Marker, *J. Biol. Chem.* 91, 699-700 (1931).

3:9554 3-CHLORO-2,3-DIMETHYLHEXANE  $C_8H_{17}Cl$  Beil. S.N. 10  
(Isopropyl-methyl-n-propyl-carbinyl chloride)



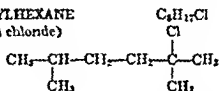
B.P. 41-43° at 12 mm. (1)

$n_D^{25} = 1.4333$  (2)  
 $D_4^{20} = 0.8809$  (1)  $n_D^{20} = 1.4353$  (2)  
1.4350 (1)

[For prepn. from 2,3-dimethylhexanol-3 [Beil. I<sub>1</sub>-(210), I<sub>2</sub>-(454)] (2) (1) with dry HCl gas at 0° (81% yield (1)) see (1) (2)]

3:9554 (1) Whitmore, Evers, *J. Am. Chem. Soc.* 55, 813-814 (1933). (2) Stevens, Greenwood, *J. Am. Chem. Soc.* 65, 2152-2153 (1913).

3:9556 2-CHLORO-2,5-DIMETHYLHEXANE  $C_8H_{17}Cl$  Beil. I —  
(Isoamyl-dimethyl-carbinyl chloride) I<sub>1</sub>-(62)  
I<sub>2</sub>—



B.P. 86° at 100 mm. (1)  
44-45° at 14 mm. (2)

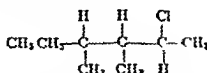
$n_D^{20} = 1.4232$ —  
1.4240 (1)  
 $D_4^{15} = 0.8470$  (2)  $n_D^{15} = 1.4205$  (2)

[For prepn. of  $\bar{C}$  from 2,5-dimethylhexanol-2 (isoamyl-dimethyl-carbinol) (2) by saturation with HCl gas (79% yield (2)) see (1) (2); for formn. of  $\bar{C}$  (together with other prods.) during hydrolysis of 2-nitroso-2,5-dimethylhexane see (1)]

[ $\bar{C}$  with  $C_6H_6$  +  $AlCl_3$  gives 2,5-dimethyl-2-phenylhexane, b.p. 116-117° at 14 mm.,  $D_4^{16} = 0.8844$ ,  $n_D^{15} = 1.50233$  (2).]

3:9556 (1) Aston, Allman, *J. Am. Chem. Soc.* 60, 1931 (1938) (2) Halse, *J. prakt. Chem.* (2) 89, 455 (1914).

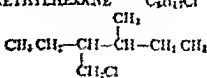
3:9558 2-CHLORO-3,4-DIMETHYLHEXANE  $C_8H_{17}Cl$  Beil. S.N. 10



No physical constants on this compound are recorded; for its formation, however, as a by-product of the addition of HCl to butene-2 see (1)

3:9558 (1) Coffin, Sutherland, Maass, *Can. J. Research* 2, 275-276 (1930).

3:9560 4-(CHLOROMETHYL)-3-METHYLHEXANE  $C_8H_{17}Cl$  Beil. S.N. 10



150° (42) (40), 149° (41);  $\bar{C}$  with acenaphthene gives (65–68% yield (43)) 5-(phenylacetyl)-acenaphthene (4-acenaphthyl benzyl ketone), m.p. 114° (43);  $\bar{C}$  with bromobenzene (in  $CS_2$ ) gives (44) 4-bromodesoxybenzoin, m.p. 114–115°, b.p. 165° at 3 mm. (44).] — [For oxidn. of many of these with  $SeO_2$  to corresp. benzils see (38).]

[ $\bar{C}$  with phenols +  $AlCl_3$  (often in nitrobenzene) similarly yields hydroxy-substituted desoxybenzoins: e.g.,  $\bar{C}$  with phenol as directed gives (60–70% yield (45)) 4-hydroxy-desoxybenzoin [Beil. VIII-165], m.p. 142° cor. (45);  $\bar{C}$  with *o*-cresol gives (60–70% yield (46)) 4-hydroxy-3-methyldesoxybenzoin [Beil. VIII-183], m.p. 152° (46);  $\bar{C}$  with salicylic acid (1:0780) gives (47) 4-hydroxy-3-carboxy-desoxybenzoin; for similar reactn. with catechol resorcinol, and hydroquinone (48) or with phloroglucinol (49) see indic. refs.]

[ $\bar{C}$  with phenol ethers +  $AlCl_3$  (often in nitrobenzene) similarly yields substituted desoxybenzoins: e.g.,  $\bar{C}$  with anisole (1:7445) +  $SnCl_4$  (61) or  $AlCl_3$  (34) (50) gives 4-methoxydesoxybenzoin [Beil. VIII-166, VIII-1-571], m.p. 77°;  $\bar{C}$  with methyl *m*-tolyl ether (1:7510) +  $SnCl_4$  (not  $AlCl_3$ ) gives (60–70% yield (51)) (50) 4-methoxy-2-methyldesoxybenzoin, m.p. 76.5° (51);  $\bar{C}$  with methyl *p*-tolyl ether (1:7495) +  $AlCl_3$  in  $CS_2$  gives (11) 2-methoxy-5-methyldesoxybenzoin, m.p. 75°, b.p. 205–207° at 14 mm. (11).]

$\bar{C}$  with phenols on htg. gives corresp. esters: e.g.,  $\bar{C}$  with phenol at 150° for 8 hrs. (6) (or  $\bar{C}$  with phenol + aq. alk. (52)) yields phenyl phenylacetate [Beil. IX-435], ndls. from lt. pet., m.p. 50° (6), 42° (52);  $\bar{C}$  with  $\beta$ -naphthol at 150° for 6 hrs. yields (6)  $\beta$ -naphthyl phenylacetate, pl. from lt. pet., m.p. 87° (6);  $\bar{C}$  with *o*-cresol at 90° yields (9) *o*-tolyl phenylacetate, m.p. 44–45° (9);  $\bar{C}$  with *m*-cresol at 90° yields (9) *m*-tolyl phenylacetate, m.p. 51–52° (9);  $\bar{C}$  with *p*-cresol at 90° yields (9) *p*-tolyl phenylacetate, m.p. 74–75° (9).

[ $\bar{C}$  with  $MeZnI$  (53) in toluene +  $EtOAc$  or with  $Me_2Zn$  (54) gives (72% yield (53)) benzyl methyl ketone (phenylacetone) (1:5118);  $\bar{C}$  with  $EtZnI$  (53) or with  $Et_2Zn$  (54) gives (78% yield (53)) benzyl ethyl ketone [Beil. VII-314, VII-1-(167)]]

[ $\bar{C}$  + *o*-hydroxyacetophenone (1:1746) +  $Na\bar{A}$  at 180° for 5 hrs. followed by hydrol. with alc. KOH gives (6) 4-methyl-3-phenylcoumarin, m.p. 163° (6);  $\bar{C}$  with 2-hydroxy-5-methylbenzophenone +  $Na\bar{A}$  at 180° gives (80–90% yield (55)) 3,4-diphenyl-6-methylcoumarin, cryst. from  $AcOH$ , m.p. 208–209° (55).]

[ $\bar{C}$  with diazomethane in ether gives acc. to cond. (56) (57) (58) (52) either (yield: 84% (55), 83% (62))  $\alpha$ -chloro- $\gamma$ -phenylacetone [Beil. VII-1-(162)], m.p. 72–73° (56), b.p. 133–135° at 19 mm. (62),  $n_D^{20} = 1.5379$  (62), or  $\alpha$ -diazo- $\gamma$ -phenylacetone (identified by reactn. with *p*-nitrobenzoic acid yielding (58)  $\alpha$ -(*p*-nitrobenzoyloxy)- $\alpha$ -phenylacetone, pl. from alc., m.p. 120° (58)); note, however, that work of (56) could not be duplicated by later investigators (68) (62).]

[ $\bar{C}$  with biuret yields (69) *N*-(phenylacetyl)biuret, cryst. from alc., m.p. 199–200° u.c. dec. (59).]

[ $\bar{C}$  with ethyl carbamate (urethane) at 60–70° gives (70% yield (60)) ethyl *N*-(phenylacetyl)carbamate, m.p. 113° (60).]

[ $\bar{C}$  with  $MeOH$  yields methyl phenylacetate (1:3771), b.p. 220°;  $\bar{C}$  with  $EtOH$  yields ethyl phenylacetate (1:3872), b.p. 227.5°.] [For use in prepn. of cellulose esters see (61).]


$\bar{C}$  on hydrolysis yields phenylacetic acid (1:0665), m.p. 76.6°; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see phenylacetic acid (1:0665)

3:9567 (1) Perkin, *J. Chem. Soc.* 69, 1205 (1896) (1931). (3) Martin, Partington, *J. Chem. Soc.* (1896). (5) Fournneau, Nicolitch, *Bull. soc. ch. Venkatarman, J. Chem. Soc.* 1933, 1461–1462.

(8) Bergs, *Ber.* 67, 240–241 (1934). (9) Raifo (1929); *Cent.* 1930, I 209. (10) Rupe, *Ann.* 363, 330 (1909).

(11) von Auwers, *Ber.* 53, 2277, 2282–2283 (1920). (12) Kohlrausch, Pongrats, *Monatsh.* 64, 382 (1934). (13) Clark, *Bell. Trans. Roy. Soc. Can.* (3) 27, III 97–103 (1933). (14) Adams,

- Ulrich, *J. Am. Chem. Soc.* 42, 601 (1920). (15) Möller, *Streckker, Ann.* 113, 68 (1860). (16) Vanino, *Thiele, Ber.* 29, 1727, Note (1895). (17) Ivanov, *Nicolov, Bull. soc. chim.* (4) 51, 1333 (1922). (18) Weiss, *Monatsh.* 40, 331-393 (1910). (19) Metzner, *Ann.* 294, 375-376 (1897). (20) Allen, Barker, *Org. Synthesis* 12, 16-18 (1932), Coll. Vol. 2 (1st ed.), 156-158 (1943). (21) Aeschliman, *J. Chem. Soc.* 1928, 2909. (22) Meyer, *Monatsh.* 22, 427-428 (1901). (23) Montonna, *J. Am. Chem. Soc.* 49, 2114-2116 (1927). (24) Rupe, *Fiedler, J. prakt. Chem.* (2) 84, 814 (1911). (25) Wedekind, *Ber.* 34, 2074-2077 (1901). (26) Durran, *J. Chem. Soc.* 121, 49 (1922). (27) Wedekind, *Ann.* 378, 262-268, 275-283 (1910). (28) Rosenmund, *Zetsche, Ber.* 54, 437 (1921). (29) Fröschl, *Dinoff, J. prakt. Chem.* (2) 144, 223-221 (1936). (30) Grignard, *Mignowin, Compt. rend.* 143, 1176 (1927). (31) von Braun, Kochenbörler, *Ber.* 36, 2176 (1923). (32) Sugawara, *Tsuda, J. Pharm. Soc. Japan* 36, 107-103 (1936), *Cent.* 1936, 11 3670. (33) Gräse, *Bungener, Ber.* 12, 1079-1080 (1879). (34) Tiffeneau, *Levy, Ditz Bull. soc. chim.* (5) 2, 1873-1874, 1875 (1935). (35) Mann, *Ber.* 14, 1646 (1881). (36) Kayser, *Ann. Chem.* (11) 6, 187-188 (1936). (37) Wege, *Ber.* 21, 3540-3542 (1891). (38) Hatt, *Pilgram, Hurran, J. Chem. Soc.* 1936, 91-93. (39) Ruggli, *Reinert, Helv. Chim. Acta* 9, 71-74 (1926). (40) Ferns, *Turner, J. Chem. Soc.* 117, 1148-1149 (1920). (41) Delaville, *Compt. rend.* 156, 463 (1927). (42) Papeke, *Ber.* 21, 1239 (1888). (43) Ruggli, *Jenny, Helv. Chim. Acta* 10, 231-232 (1927). (44) Speer, *Hill, J. Org. Chem.* 2, 142 (1937). (45) Weid, *Monatsh.* 26, 986-987 (1905). (46) Blau, *Monatsh.* 26, 1151-1153 (1905). (47) Glaser, *Monatsh.* 29, 282-285 (1907). (48) Finas, *Monatsh.* 26, 1119-1128 (1905). (49) K. Rosenmund, *M. Rosenmund, Ber.* 61, 2610 (1928). (50) Ney, *Ber.* 21, 2450-2451 (1888). (51) Hill, *Short, J. Chem. Soc.* 1935, 1125. (52) Stoeckner, *Breunbach, Ber.* 38, 1962 (1905). (53) Morgan, *Drew, Porter, Ber.* 58, 339-341 (1925). (54) Popov, *J. Russ. Phys.-Chem. Soc.* 4, 214 (1872); *Ber.* 6, 508-502 (1873). (55) Ziesler, *Fries, Salzer, Ann.* 448, 261 (1926). (56) Childens, *Nierenstein, J. Chem. Soc.* 107, 1492 (1915). (57) Lewis, *Nierenstein, Rich, J. Am. Chem. Soc.* 47, 1729 (1925). (58) Bradley, *Schwarzenbach, J. Chem. Soc.* 1928, 2906. (59) Ostrogovich, *Tanikau, Gazz. chim. ital.* 64, 825-828 (1934), *Cent.* 1935, 1 2820. (60) Basterfield, *Woods, Wright, J. Am. Chem. Soc.* 48, 2371-2372 (1926). (61) I. G. Hitt, 305, 347, April 10, 1929, *Cent.* 1929, 11 112. (62) Melther, *Klingenberg, J. Am. Chem. Soc.* 66, 1131-1135 (1944).

3:9570 ***dl*-CHLOROMETHYL-PHENYL-CARBINOL**  $C_8H_9OCl$  **Beil. V7 —**  
 ( $\beta$ -hydroxy- $\beta$ -phenylethyl chloride,  $H$  **VI<sub>1</sub>-(276)**  
 $\alpha$ -chloromethylbenzyl alcohol,  **CH<sub>2</sub>** **VI<sub>2</sub>-(416)**  
 styrene chlorohydrin) **OHCl**

**B.P.** 128° at 17 mm. (1)  $n_D^{25} = 1.5538$  (2)  
 118-126° at 16 mm. (2) 1.5520 (2)  
 112-114° at 10 mm. (3)  $D_4^{25} = 1.1616$  (1)  $n_D^{25} = 1.5100$  (1)  
 110-111° at 6 mm. (4)  
 110-112° at 5 mm. (5)  $D_4^{25} = 1.223$  (1)  $n_D^{25} = 1.55103$  (1)

(For prepn. of  $\bar{C}$  from phenylethylene (styrene) (1 7135) by addition of HOCl generated from  $Ca(OCl)_2$  +  $CO_2$  (76% yield (2)), from  $NaOCl$  +  $CO_2$  (6), from  $N$ -chlorosuccinimide +  $AcOH$  (yield: 70% (1), 52% (4)), or from *tert*-butyl hypochlorite (3 7165) in dil.  $AcOH$  (60-70% yield (1)) see indie. refs. (note that conversion of  $AcOH$  in *tert*-BuOCl method leads to 1 min. by direct addn. (4) of chloromethyl-phenylbenzyl *tert*-butyl ether, b.p. 87-88° at 1.5 mm.,  $D_4^{25} = 1.0519$ ,  $n_D^{25} = 1.5102$  (4))

(For prepn. of  $\bar{C}$  from chloromethylolide (1 7212) with  $C_6H_5MgBr$  in ether (71% yield (1)) or from  $\alpha$ , $\beta$ -dichlorophenylethane (styrene dichloride) (1 6682) with a mild dehydrochlorinating agent such as  $Na_2CO_3$ ,  $NaOAc$ ,  $CaO$ , or  $CaCO_3$  (not an alkali hydroxide) and methyl (2) see indie. refs.]

( $\bar{C}$  with a)  $KOH$  (1) or with an alk. or alk. earth metal oxide or hydroxide as directed (5) (6) or with  $HCl$  with neg. charge to phenylethylolane (styrene oxide) (Beil. XVII-49 of Cl, b.p. 191-192°, but no phenylmethylolide (1 6200) is formed (1) (for use of this

conversion to remove  $\bar{C}$  from mixtures with styrene dichloride (3:6685) see (7) (8).—However,  $\bar{C}$  with NaOEt gives (yield not reported (1)) cf. (3) ethyl  $\beta$ -hydroxy- $\beta$ -phenylethyl ether [Beil. VI-907], h.p. 242–243°.]

[C on dehydration by passing over  $\text{HPO}_3$  on silica gel at 370–400° and 95–115 mm. press. gives (63% yield (9))  $\beta$ -chlorostyrene (3:8717).]

[ $\bar{C}$  on passing over activated  $Al_2O_3$  at 360–390° and 115–125 mm. press. gives (67% yield (9)) acetophenone (1:5515), but  $\bar{C}$  on passing over  $CaCO_3$  on silica gel at 325–350° and 105–125 mm. press. gives (51% yield (9)) phenylacetaldehyde (1:0200).]

$\bar{C}$  with pyridine at 120° for 6 hrs. gives in quant. yield (10) the corresp. quaternary pyridinium salt; m.p. 210–212° dec., sol. in aq., MeOH, EtOH, but spar. sol. in other org. solvents.

$\bar{C}$  on oxidn. with  $K_2Cr_2O_7/H_2SO_4/AcOH$  at low temp. (1) cf. (4) gives (84% yield (4))  $\omega$ -chloroacetophenone (phenacyl chloride) (3:1212).

—Chloromethyl-phenyl-carbinyl acetate: b.p. 101–104° at 3 mm.,  $n_D^{25} = 1.5182$  (4).  
[From **C** with  $\text{Ac}_2\text{O}$  + pyridine (66% yield (4)).]

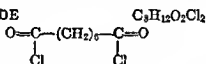
— Chloromethyl-phenyl-carbinyl benzoate: unreported.

① Chloromethyl-phenyl-carbinyl *p*-nitrobenzoate: m.p. 81° (4). [From **C** with *p*-nitrobenzoyl chloride in pyridine (4).]

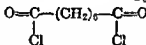
— Chloromethyl-pbenyl-carbinyl 3,5-dinitrobenzoate: unreported.

3: 9570 (1) Detoef, *Bull. soc. chim.* (4) 31, 176-177 (1922). (2) Emerson, *J. Am. Chem. Soc.* 67, 516-518 (1945). (3) Späth, *Monatsh.* 36, 6-7 (1915). (4) Hanhy, Rydon, *J. Chem. Soc.* 1946, 114-115. (5) I.G., French 735,108, Nov. 3, 1932; *Cent.* 1933, II 1093; *C.A.* 27, 1011 (1938). (6) Esser, Ward (to du Pont Co), U.S. 1,594,608, Aug. 3, 1926; *Cent.* 1926, II 1693; *C.A.* 29, 3170 (1926). (7) I.G., Brit. 381,459, Oct. 27, 1932; *Cent.* 1933, I 506; *C.A.* 27, 3950 (1938). (8) Knorr (to I.G.) Ger. 559,521, Sept. 21, 1932; *Cent.* 1933, I 1843; *C.A.* 27, 736 (1933); French 735,000, Oct. 31, 1932; *Cent.* 1933, I 1843; *C.A.* 27, 1011 (1933). (9) Emerson, Agnew, *J. Am. Chem. Soc.* 67, 518-520 (1945). (10) Gautier, *Compt. rend.* 193, 1430-1431 (1934).

## 3:9576 SUBERYL (DI)CHLORIDE



Beil. II - 694



II<sub>1</sub>-(287)

И<sub>2</sub>-(596)

B.P. 162-163° at 15 mm., sl. dec. (1)

159–160° at 12 mm. (2)

149–150° at 12 mm. (3)

147° at 12 mm. (4)

143-147° at 12 mm. (5)

$$D_1^{208} = 1.1718(3) \quad n_D^{208} = 1.46847(3)$$

[For prepn. of  $\tilde{C}$  from suberic acid (I:0755) with  $PCl_5$  (1), with  $PCl_3$  (4), or with  $SOCl_2$  (yield: 100% (2) (3) (5) (6) (8) (10) see indic. refs.)

[C with excess MeOH yields (6) dimethyl suberate (I:4186), b.p. 268°. C with 1 mole MeOH should yield 7-carhomethoxyheptanoyl chloride-1, b.p. 163-165° at 34 mm. (7), usually prep'd. from methyl hydrogen suberate with  $\text{SOCl}_2$  (7).]

$\bar{C}$  with excess phenol htd. at 100° yields (8) diphenyl suberate, m p. 70–71° (8).

With dry disodium suberate yields (I) suberic anhydride, m.p. 65–66° (I), presumably the linear polymeric suberic  $\alpha$ -anhydride (cf. 1:0755).

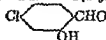
$\bar{C}$  with  $AlCl_3$  +  $C_6H_6$  yields (I) (4) 1,8-diphenyloctanedione-1,8, m.p.  $85^\circ$  (4),  $83-85^\circ$  (I) (dioxime, m.p.  $192-193^\circ$  (1)).

[C on cat. hydrogenation over Pd/diatomaceous earth as directed (9) yields suberic dialdehyde (octanedial-1,8), (*bis*-oxime, m.p. 152° (9), *bis*-phenylhydrazone, m.p. 84–86° u.c. (9), *bis*-semicarbazone, m.p. 183–185° (9)) cf. (2).]

$\bar{C}$  converted to  $\text{RMgCl}$  (as above) and treated with ethereal  $\text{HgCl}_2$  gives (35% yield) (1) 2,2,3,3-tetramethylbutyl mercuric chloride, feathery white cryst., m.p.  $170-171^\circ$  (1).

3:0945 (1) Whitmore, Marker, Plambeck, *J. Am. Chem. Soc.* 63, 1626-1630 (1941).

3:0960 4-CHLORO-2-HYDROXYBENZALDEHYDE  $\text{C}_7\text{H}_5\text{O}_2\text{Cl}$  Beil. No. 744  
(4-Chlorosalicylaldehyde)



M.P.  $52.5^\circ$  (1)

Long colorless ndls. from alc. or dil.  $\text{AcOH}$  (1). —  $\bar{C}$  has odor of walnuts (1). —  $\bar{C}$  is apprec. sol. in aq. or aq.  $\text{H}_2\text{SO}_3$ ; readily sol. in org. solvents. —  $\bar{C}$  is very volatile with steam even from its yel. soln. in alk. (1).

[For prepn. of  $\bar{C}$  from *m*-chlorophenol (3.0255) via Reimer-Tiemann procedure see (1).]

$\bar{C}$  does not reduce  $\text{NH}_4\text{OH}/\text{AgNO}_3$  or Fehling soln.; is very resistant to oxidn. by acid, alk., or neutral  $\text{KMnO}_4$ , and to acetylation (but not benzylation, q.v. below) (1).

$\bar{C}$  with  $\text{FeCl}_3$  gives brown ppt., with  $\text{CuSO}_4$  or  $\text{Cr}_2(\text{SO}_4)_3$  + dil. aq. alk. gives bright green copper salt and a dark green chromium salt (1).

$\bar{C}$  on mononitration as specified (2) yields 5-nitro-4-chloro-2-hydroxybenzaldehyde, pale yel. ndls. from alc., m.p.  $116^\circ$  (2) [This product yields a phenylhydrazone, or.-yel. ndls., m.p.  $188^\circ$  dec.; a *p*-nitrophenylhydrazone, brn.-yel. ndls. from alc. or  $\text{AcOH}$ , m.p.  $204^\circ$  dec.; and a semicarbazone, pale yel. ndls. from dil.  $\text{AcOH}$ , dec. above  $300^\circ$  (2).]

$\bar{C}$  on dinitration as specified (2) yields 3,5-dinitro-4-chloro-2-hydroxybenzaldehyde, pale gold.-yel. ndls. from aq., m.p.  $153^\circ$  (2). [This product yields a phenylhydrazone, light brn. cryst. from alc., m.p.  $219^\circ$ ; a *p*-nitrophenylhydrazone, light brn. cryst. from dil.  $\text{AcOH}$ , m.p.  $236^\circ$  dec.; and a semicarbazone, light yel. cryst. from dil.  $\text{AcOH}$ , m.p.  $225^\circ$  dec. (2).]

① 4-Chloro-2-hydroxybenzaldehyde: colorless ndls. from alc., m.p.  $155^\circ$  (1).

② 4-Chloro-2-hydroxybenzaldehyde *p*-nitrophenylhydrazone: or. ndls. from  $\text{AcOH}$ , m.p.  $257^\circ$  (1).

③ 4-Chloro-2-hydroxybenzaldehyde semicarbazone: pale yel. cryst. from  $\text{AcOH}$ , m.p.  $212^\circ$  (1).

④ 4-Chloro-2-benzoylbenzaldehyde: from  $\bar{C}$  +  $\text{BzCl}$  in ether + pyridine; ndls. from alc., m.p.  $98.5^\circ$  (1)

3:0960 (1) Hodgson, Jenkinson, *J. Chem. Soc.* 1927, 1740-1741. (2) Hodgson, Jenkinson, *J. Chem. Soc.* 1928, 2273-2274.

3:9590 8-CHLORO-OCTANOL-1  $\text{CH}_2(\text{CH}_2)_6\text{CH}_2\text{OH}$   $\text{C}_8\text{H}_{17}\text{OCl}$  Beil. S.N. 24  
 ( $\omega$ -Chloro-*n*-octyl alcohol)  
 $\begin{array}{c} | \\ \text{Cl} \end{array}$

B.P. 139° at 18.5 mm. (1)

125-140° at 18 mm. (2)

[For prepn. of  $\bar{\text{C}}$  from  $\alpha, \omega$ -octamethylene glycol (m.p. 63°, b.p. 167-168° at 18 mm. (2)) with conc. HCl as directed (yields: 81% (2), 75% (1), 65% (3)) see indic. refs.]

$\bar{\text{C}}$  with thiophenol in aq. NaOH htd. 3 hrs. gives (2) 8-hydroxy-*n*-octyl phenyl sulfide, pl from lt. pet., m.p. 55° [this prod. with  $\text{SOCl}_2$  gives (2) 8-chloro-*n*-octyl phenyl sulfide, cryst. from aq. alc. at low temp., m.p. 16°].

[ $\bar{\text{C}}$  (1 mole) with  $\text{Et}_3\text{NH}$  (3-4 moles) in s.t. at 120-160° for 12-15 hrs. gives (88% yield (1)) 8-(diethylamino)octanol-1, b.p. 151° at 12 mm.,  $D_4^{15.5} = 0.8610$ ,  $n_D^{19} = 1.4570$  (1) cf. (5) (corresp. *p*-nitrobenzoate, m.p. 74° (1)); this prod. with  $\text{SOCl}_2$  in  $\text{C}_6\text{H}_6$  yields (1) (5) 8-(diethylamino)-*n*-octyl chloride, b.p. 130.5° at 11 mm.,  $n_D^{18} = 1.4535$  (1) cf. (5) (corresp.  $\bar{\text{B}}\cdot\text{HCl}$ , m.p. 73° (5)).]

$\bar{\text{C}}$  with morpholine gives (4) alm. quant. 8-(4-morpholinyl)octanol-1, b.p. 164.0-164.2° at 5 mm.,  $D_4^{25} = 0.9675$ ,  $n_D^{27} = 1.4735$  (corresp. *N*-( $\alpha$ -naphthyl)carbamate, m.p. 73.0-74.0° cor.) —  $\bar{\text{C}}$  (1 mole) with *N*-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (3) in alm. 100% yield (as salt) *N*-(8-hydroxy-*n*-octyl)-*N'*-phenylpiperazine, m.p. 57.0-58.5° cor. (corresp. *N*-phenylcarbamate, m.p. 99.5-100.5° cor.) note that this free base readily absorbs aq. from air to form a monohydrate, m.p. 80-82° (3).

① 8-Chloro-*n*-octyl *N*-phenylcarbamate: ndls from aq. alc., m.p. 77° (2).

② 8-Chloro-*n*-octyl *N*-(*m*-nitrophenyl)carbamate: m.p. 62° (1).

3:9590 (1) Altman, *Rec. trav. chim.* 57, 951-952 (1938). (2) Bennett, Mosses, *J. Chem. Soc.* 1931, 1698-1701. (3) Anderson, Pollard, *J. Am. Chem. Soc.* 61, 3439-3440 (1939). (4) Anderson, Pollard, *J. Am. Chem. Soc.* 61, 3440-3441 (1939). (5) Pyman, Levene (to Boot's Pure Drug Co.), Brit. 402,159, Dec. 21, 1933; *Cent.* 1934, I 2005, *C.A.* 28, 3081 (1034).

3:9594  $\beta$ -CHLORO-*n*-BUTYRALDEHYDE  $\text{C}_4\text{H}_7\text{O}_2\text{Cl}$  Beil. I - 663  
 DIETHYLACETAL  $\text{CH}_3\text{CH}(\text{CH}_2\text{CH}(\text{OC}_2\text{H}_5)_2)$  I<sub>1</sub>—  
 ( $\beta$ -Chlorobutyralactal)  $\begin{array}{c} | \\ \text{Cl} \end{array}$  I<sub>2</sub>-(724)

B.P. 70-71° at 12 mm. (1)

$D_4^{20} = 0.9677$  (2)  $n_D^{20} = 1.42103$  (2)

Oil insol. aq.; misc. with alc.,  $\text{C}_6\text{H}_6$ , AcOH, or  $\text{CHCl}_3$  or pet. ether.

[For prepn. of  $\bar{\text{C}}$  from crotonaldehyde (1:0150) with abs. EtOH + dry HCl (yield: 66% (1), 50% (3)) (2) see indic. refs.]

$\bar{\text{C}}$  on distn. with dry KOH gives (70-80% yield) crotonaldehyde diethylacetal [Beil. I-730, I<sub>1</sub>-(380), I<sub>2</sub>-(789)], b.p. 146-148°.

[For reactn. of  $\bar{\text{C}}$  with alc.  $\text{NH}_3$  in s.t. at 120-130° giving (20% yield (4))  $\beta$ -amino-*n*-butyraldehyde diethylacetal see (4); for analogous behavior of  $\bar{\text{C}}$  with other amines see (4) (3).]

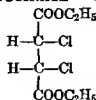
3:9594 (1) Wohl, Frank, *Ber.* 35, 1905-1906 (1902). (2) Wichterle, Vavrecka, *Collection Czechoslov. Chem. Commun.* 10, 494 (1938). (3) Mason, *J. Chem. Soc.* 127, 1033 (1925). (4) Mannich, Horkheimer, *Arch. Pharm.* 264, 171-172 (1926).

$\bar{C}$  treated with  $Br_2$ , then poured into abs. formic acid and boiled until evolution of  $CO$  ceases, yields (10)  $\alpha, \alpha'$ -dibromosuberic acid, m.p.  $172-173^\circ$  (10). [From the mother liq. a small amt. of another form, m.p.  $120-121^\circ$  (10), can be obt'd.]

$\bar{C}$  on hydrolysis yields suberic acid (1:0755), m.p.  $141^\circ$  (for the diamide, dianilide, di-*p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see 1:0755).

3:9576 (1) Etaix, *Ann. chim.* (7) 9, 336-391 (1896). (2) Fröschl, Maier, *Monatsh.* 59, 273-274 (1932). (3) von Auwers, Schmidt, *Ber.* 46, 479 (1913). (4) Borsche, Wolleman, *Ber.* 45, 3717 (1912). (5) Blaise, Koehler, *Bull. soc. chim.* (4) 5, 690 (1909). (6) Meyer, *Monatsh.* 22, 421 (1901). (7) Morgan, Walton, *J. Chem. Soc.* 1935, 292. (8) Marangoni, *Atti ist. Veneto sci. Pt. 2. Sci. math. nat.* 97, 209-218 (1937-1938). *Cent.* 1939, 196; *C.A.* 34, 6934-6935 (1940). (9) Rosenmund, *Zetsche, Ber.* 54, 2889-2890 (1921); (10) Goss, Ingold, *J. Chem. Soc.* 1926, 1473.

3:9578 DIETHYL *d,l*- $\alpha, \alpha'$ -DICHLOROSUCCINATE  $C_8H_{12}O_4Cl_2$  Beil. II - 620  
(Diethyl *allo*-dichlorosuccinate;  
diethyl isodichlorosuccinate)



$\Pi_1$ —  
 $\Pi_2$ -(558)

B.P.  $132^\circ$  cor. at 15 mm. (1)  
 $129.5^\circ$  at 12.5 mm. (1)

$D_4^{20} = 1.1636$  (1)  $n_D^{64.5} = 1.4296$  (1)  
 $D_4^{77} = 1.1063$  (1)  $n_D^{20} = 1.4512$  (1)  
 $n_D^{17.5} = 1.4521$  (1)

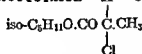
Stable oil (1), contrary to earlier (2) report.

[For prepn. of  $\bar{C}$  from *d,l*- $\alpha, \alpha'$ -dichlorosuccinic acid (3:4711) in EtOH with HCl gas see (1) cf. (2).]

$\bar{C}$  with 30%  $H_2SO_4$  on boilg. not only hydrolyzes but also loses HCl yielding (3) chloro-fumaric acid (3:4853).

3:9578 (1) Kuhn, Wagner-Jauregg, *Ber.* 61, 485-486, 504 (1928). (2) van der Riet, *Ann.* 280, 221 (1894). (3) Patterson, Todd, *J. Chem. Soc.* 1929, 1769-1770.

3:9580 ISOAMYL *d,l*- $\alpha$ -CHLOROPROPIONATE  $C_8H_{16}O_2Cl$  Beil. S.N. 162

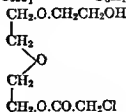


B.P.—

$D_4^{20} = 1.0059$  (1)  $n_D^{20} = 1.4289$  (1)

3:9580 (1) Schjanberg, *Z. physik. Chem. A*-172, 231 (1935).

3:9588  $\beta$ -( $\beta$ -HYDROXYETHOXY)ETHOXY- $\alpha$ -ETHYL CHLOROACETATE  $C_8H_{16}O_5Cl$  Beil. S.N. 160  
[Triethylene glycol  
mono(chloroacetate)]



B.P.  $180-195^\circ$  at 0.5 mm. (1)

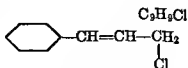
Viscous oil, insol. in aq. but slowly dissolving when shaken with aq. because of hydrolysis to triethylene glycol (1:6538) + chloroacetic ac. (3:1370) (1).

3:9588 (1) Meerwein, Sönke, *J. prakt. Chem.* (2) 137, 317 (1933).



## CINNAMYL CHLORIDE

(3-Chloro-1-phenylpropene-1)

 $C_9H_9Cl$ 

Beil. V -(482)

V<sub>1</sub>-(232)V<sub>2</sub>-(372)

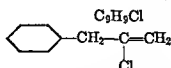
B.P. 140° at 37 mm.

M.P. 8-9°

 $D_4^{25} = 1.08815$  $n_D^{25} = 1.58065$ 

See 3:0010. Division A: Solids.

## 3:9608 2-CHLORO-3-PHENYLPROPENE-1

 $C_9H_9Cl$ 

Beil. S.N. 473

B.P. 105-107° at 26 mm. (1)

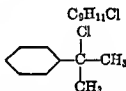
[For prepn. of  $\bar{C}$  from benzyl methyl ketone (phenylacetone) (1:5118) with  $PCl_5$  in  $C_6H_6$  (yield 45.9% accompanied by 26.3% of the mesomeric 2-chloro-1-phenylpropene-1 (3:9606)) see (1).]

$\bar{C}$  on stdg. isomerizes in part to the mesomeric 2-chloro-1-phenylpropene-1 (3:9606)(1).

$\bar{C}$  (freshly distilled) with  $O_3$  in  $CHCl_3$  contg. some EtOH yields (1) ethyl phenylacetate (1:3872) (note difference from the mesomer).

3:9608 (1) Zaki, Iskander, *J. Chem. Soc.* 1943, 68-69.3:9610  $\alpha$ -CHLORO-ISOPROPYLBENZENE

(Dimethyl-phenyl-carbinyl chloride; 2-chloro-2-phenylpropane)

 $C_9H_{11}Cl$ 

Beil. V - 395

V<sub>1</sub>-V<sub>2</sub> - (307)

No physical constants for  $\bar{C}$  appear to have been reported, presumably because of its ease of decomposition.

[For prepn. of  $\bar{C}$  from dimethyl-phenyl-carbinol [Beil. VI-506] by saturation with dry HCl gas at 0° see (1) (2).]

$\bar{C}$  on htg. evolves HCl (1). —  $\bar{C}$  in  $C_6H_6$  +  $SnCl_4$  stood for several hours below 10° gives (88% yield) the "saturated dimer of  $\alpha$ -methylstyrene," i.e., 1,1,3-trimethyl-3-phenyl-hydrindene, cryst. from alc., m.p. 52° (3).

$\bar{C}$  on slow addn. to boilg. alc. KOH (4) or on warming with pyridine (1) (4) loses HCl smoothly giving (70% yield (5))  $\alpha$ -methylstyrene ( $\beta$ -phenylpropylene) [Beil. V-484, V<sub>1</sub>-(233)], b.p. 161-162° (5).

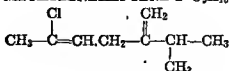
$\bar{C}$  dislvd. in MeOH and merely stood overnight gives (6) the corresponding ether, viz., 2-methoxy-2-phenylpropane, b.p. 78° at 13 mm.,  $D_4^{20} = 0.945$ ,  $n_D^{20} = 1.4981$  (6).

2546 (1929). (3)

i. (8) 10, 156-157

4-255 (1924).

## 3:9614 2-CHLORO-6-METHYL-5-METHYLENEHEPTENE-2

 $C_9H_{15}Cl$  Beil. S.N. 10

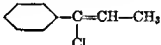
B.P. 95-96° at 18 mm. (1)

 $D_4^{25} = 0.0310$  (1)  $n_D^{25} = 1.4730$  (1)

## CHAPTER XXII

### DIVISION C. LIQUIDS WITH BOILING POINTS REPORTED ONLY UNDER REDUCED PRESSURE

3:9600-3:9999 (C<sub>9</sub>-C<sub>18</sub> inclusive)  
(Arranged in sequence of empirical formulas)

3:9604 1-CHLORO-1-PHENYLPROPENE-1 C<sub>9</sub>H<sub>9</sub>Cl Beil. V —  
( $\alpha$ -Chloro- $\beta$ -methylstyrene)  V<sub>1</sub>-(232)  
V<sub>2</sub>-(372)

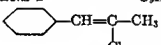
B.P. 90.5° at 9 mm. (1)

$$D_4^{20} = 1.085 \quad (1) \\ D_4^{14.6} = 1.0890 \quad (1) \quad n_D^{14.6} = 1.56352 \quad (1)$$

[For prepn. of  $\bar{C}$  from ethyl phenyl ketone (propiophenone) (1:5525) by treatment with PCl<sub>5</sub> followed by alc. KOH see (1) ]

[ $\bar{C}$  with NaNH<sub>2</sub> in toluene at 110° gives traces (2) of methyl-phenyl-acetylene [Beil. V-514, V<sub>2</sub>-(408)] ]

3:9604 (1) von Auwers, *Ber.* 45, 2799-2801 (1912). (2) Bourgeul, *Ann. chim.* (10) 3, 351 (1925).

3:9606 2-CHLORO-1-PHENYLPROPENE-1 C<sub>9</sub>H<sub>9</sub>Cl Beil. S.N. 473  
( $\beta$ -Chloro- $\beta$ -methylstyrene) 

B.P. 118-123° at 28 mm. (1)

120-124° at 26 mm. (2)

61.5-62.5° at 2 mm. (3)

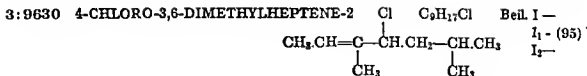
$$D_4^{19} = 1.0738 \quad (3) \quad n_D^{19} = 1.5565 \quad (3) \\ D_4^0 = 1.0912 \quad (3)$$

[For prepn. of  $\bar{C}$  from benzyl methyl ketone (phenylacetone) (1:5118) with PCl<sub>5</sub> in C<sub>6</sub>H<sub>6</sub> (26.3% yield accompanied by 45.9% of the mesomeric 2-chloro-3-phenylpropene-1 (3:9608)) see (2); from 2,3-dichloro-1-phenylpropene-1 (3) by partial reduction with Zn dust in EtOH under N<sub>2</sub> (70% yield accompanied by 16-20% 1-phenylpropadiene-1,2 (phenylallene)) see (3); for formn. as by-prod. during addn. of HOCl to  $\alpha$ -methylcinnamic acid see (1).]

Note that  $\bar{C}$  on stdg. isomerizes in part (2) to the mesomeric 2-chloro-3-phenylpropene-1 (3:9608).

$\bar{C}$  (freshly distilled) with O<sub>3</sub> in CHCl<sub>3</sub> gives (2) benzoic acid (1:0715);  $\bar{C}$  on oxidn. with KMnO<sub>4</sub> yields (3) benzoic acid (1:0715) + AcOH (1:1010) (note difference from the mesomer).

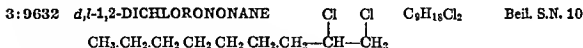
3:9606 (1) Hose, Farmer, *J. Chem. Soc.* 1933, 965. (2) Zaki, Iskander, *J. Chem. Soc.* 1943, 68-69 (3) Ginzburg, *J. Gen. Chem. (U.S.S.R)* 8, 1029-1041 (1938); *Cent.* 1939, I 2183; *C.A.* 33, 3776 (1939).



B.P. 59–63° at 9 mm. (1)

[For prepn. of  $\bar{\text{C}}$  from 2,5-dimethylhepten-5-ol-4 [Beil. I<sub>1</sub>-(231)] with 6 N HCl (78% yield) see (1).] -

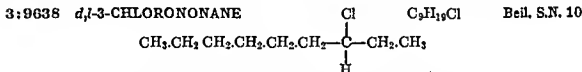
3:9630 (1) Abelman, *Ber.* 43, 1582 (1910).



No data on  $\bar{\text{C}}$  have apparently been reported.

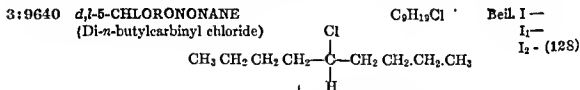
[For prepn. of  $\bar{\text{C}}$  from nonene-1 (1:8385) by actn. of HOCl (together with 1-chlorononanol-2) see (1).]

3:9632 (1) Kiss (to Shell Development Co.), U.S. 1,767,291, June 24, 1930; *Cent.* 1930, II 1475.



$\bar{\text{C}}$  has not as yet been reported, although both the optical isomerides are known. The dextrorotatory form of  $\bar{\text{C}}$ , from levorotatory nonanol-3 with HCl at 100° (1), or from levorotatory 3-iodononane with LiCl in MeOH (2), has b.p. 98° at 33 mm. (2), 87–89° at 24 mm. (1),  $D_4^{17} = 0.8558$  (1). The levorotatory form of  $\bar{\text{C}}$ , from dextrorotatory nonanol-3, with HCl at 100° (1), has b.p. 101° at 40 mm.,  $D_4^{17} = 0.8540$  (1).

3:9638 (1) Pickard, Kenyon, *J. Chem. Soc.* 99, 71 (1911). (2) Levene, Rothen, Kuna, *J. Biol. Chem.* 120, 786 (1937).

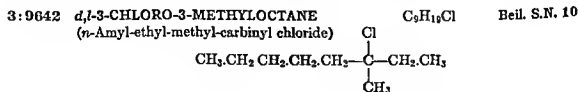


B.P. 85–87° at 14 mm. (1)

$D_4^{15} = 0.8639$  (1)  $n_D^{15} = 1.4314$  (1)

[For prepn. of  $\bar{\text{C}}$  from 5-bromononane by conversion to RMgBr and subsequent treatment with Cl.CN (68% yield) see (1).]

3:9640 (1) Grignard, Ono, *Bull. soc. chim.* (4) 39, 1592 (1926).



B.P. 72.7–74.0° at 15 mm. (1)

$D_4^{25} = 0.8680$  (1)  $n_D^{25} = 1.4330$  (2)  
 $n_D^{20} = 1.4351$  (2)  
 1.4347 (1)

[For prepn. of  $\bar{C}$  from 2-methyl-3-methyleneheptanone-6 (thujaketone) [Beil. I-745, I<sub>1</sub>-(386)] with  $\text{PCl}_5$  in the cold, then htd. at  $100^\circ$  for  $2\frac{1}{2}$  hrs. (40% yield), see (1).]

$\bar{C}$  on oxidn. with  $\text{KMnO}_4$  yields (1) 2-methylbutanone-3 (isopropyl methyl ketone) (1:5410) q.v.

3:9614 (1) Werner, Bogert, *J. Org. Chem.* 3, 585 (1939).

3:9618 1-CHLORONONYNE-1  $\text{Cl}$   $\text{C}_9\text{H}_{15}\text{Cl}$  Beil. S.N. 12  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$

B.P.  $75-77^\circ$  at 15 mm. (1)  $D_4^{20} = 0.006$  (1)  $n_D^{20} = 1.450$  (1)

[For prepn. of  $\bar{C}$  from nonyne-1 (1:8125) by conversion with  $\text{NaNH}_2$  to  $\text{C}_7\text{H}_{15}-\text{C}\equiv\text{C}-\text{Na}$  and subsequent reactn. with benzenesulfonyl chloride in dry ether (55% yield (1)) see (1).]

[Refractive indices of  $\bar{C}$  by Pulfrich instrument:  $n_D^{13} = 1.4492$ ,  $n_D^{13} = 1.4519$ ,  $n_F^{13} = 1.4582$ ,  $n_G^{13} = 1.4634$  (1).]

3:9618 (1) Truchet, *Ann. chim.* (10) 16, 335, 337 (1931).

3:9622 *d,l*-2-CHLORO-2-METHYLOCTYNE-3  $\text{Cl}$   $\text{C}_9\text{H}_{15}\text{Cl}$  Beil. S.N. 12  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}\equiv\text{C}-\underset{\text{CH}_3}{\overset{\text{Cl}}{\text{C}}}-\text{CH}_3$

B.P.  $68^\circ$  at 15 mm. (1)  $D_4^{20} = 0.8929$  (1)  $n_D^{20} = 1.4480$  (1)

[For prepn. of  $\bar{C}$  from 2-methyloctyn-3-ol-2 (1) by saturation with  $\text{HCl}$  gas (85% yield) see (1).]

[ $\bar{C}$  with  $\text{MeMgBr}$  gives 74% yield 2,2-dimethyloctyne-3, b.p.  $79^\circ$  at 70 mm.,  $D_4^{20} = 0.7401$ ,  $n_D^{20} = 1.4270$  (1);  $\bar{C}$  with  $\text{EtMgBr}$  gives 60% yield 3,3-dimethylnonyne-4, b.p.  $82^\circ$  at 40 mm.,  $D_4^{20} = 0.7650$ ,  $n_D^{20} = 1.4312$  (1).]

3:9622 (1) Campbell, Eby, *J. Am. Chem. Soc.* 62, 1799-1800 (1940).

3:9624 5-CHLORO-4-METHYLOCTENE-3  $\text{Cl}$   $\text{CH}_3$   $\text{C}_9\text{H}_{17}\text{Cl}$  Beil. I —  
 $\text{CH}_2\text{CH}_2\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{Cl}}{\text{CH}}}-\text{C}=\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3$  I<sub>1</sub> - (95)  
 I<sub>2</sub> —

B.P.  $59-62^\circ$  at 11 mm. (1)

[For prepn. of  $\bar{C}$  from 4-methylocten-3-ol-5 [Beil. I<sub>1</sub>-(230), I<sub>2</sub>-(492)] with conc.  $\text{HCl}$  see (1).]

3:9624 (1) Bjelouss, *Ber.* 45, 626 (1912).

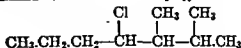
3:9628 *d,l*-4-CHLORO-7-METHYLOCTENE-2  $\text{C}_9\text{H}_{17}\text{Cl}$  Beil. I - 223  
 (Isoamyl-propenyl-carbinyl  
 chloride; 5-chloro-2-  
 methyloctene-6)  $\text{CH}_3\text{CH}=\text{CH}-\underset{\text{H}}{\overset{\text{Cl}}{\text{CH}}}\cdot\text{CH}_2\text{CH}_2-\underset{\text{H}}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_3$  I<sub>1</sub> —  
 I<sub>2</sub> —

B.P.  $124-126^\circ$  at 108 mm. (1)

[For prepn. of  $\bar{C}$  from 2-methylocten-6-ol-5 (isoamyl-propenyl-carbinol) [Beil. I-449, I<sub>1</sub>-(230), I<sub>2</sub>-(492)] with  $\text{PCl}_5$  see (1).]

3:9628 (1) Reif, *Ber.* 41, 2740, 2743, Note 1 (1908).

- 3:9650 3-CHLORO-2,3-DIMETHYLHEPTANE  $\text{C}_9\text{H}_{19}\text{Cl}$  Beil. S.N. 10  
 (*n*-Butyl-isopropyl-methyl-  
 carbanyl chloride)



B.P. 54° at 8 mm. (1)

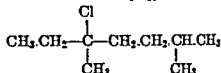
$$D_4^{23} = 0.8809 \text{ (1)}$$

$$D_4^{20} = 0.885 \text{ (1)} \quad n_D^{20} = 1.4391 \text{ (1)}$$

[For prepn. of  $\bar{C}$  from 2,3-dimethylheptanol-3 (*n*-butyl-isopropyl-methyl-carbinol) (1) with dry HCl at 0° (86% yield) see (1).]

3:9650 (1) Whitmore, Evers, *J. Am. Chem. Soc.* 55, 813 (1933).

- 3:9652 *d,l*-5-CHLORO-2,5-DIMETHYLHEPTANE  $\text{C}_9\text{H}_{19}\text{Cl}$  Beil. I-  
 (Ethyl-isoamyl-methyl-carbinyl  
 chloride) I<sub>1</sub>-(64)  
 I<sub>2</sub>-



B.P. 63-64° at 15 mm. (1)

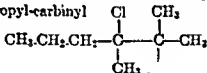
$$D_4^{18.5} = 0.8692 \text{ (1)} \quad n_D^{15} = 1.43457 \text{ (1)}$$

[For prepn. of  $\bar{C}$  from 2,5-dimethylheptanol-5 (ethyl-isoamyl-methyl-carbinol) [Beil. I-425, I<sub>1</sub>-(212)] by saturation with dry HCl gas (75% yield (1)) see (1).]

[ $\bar{C}$  with  $\text{AlCl}_3 + \text{C}_6\text{H}_6$  yields (1) 5-phenyl-2,5-dimethylheptane, b.p. 122-123° at 14 mm,  $D_4^{18} = 0.8788$ ,  $n_D^{15} = 1.49894$  (1).]

3:9652 (1) Halse, *J. prakt. Chem.* (2) 89, 455 (1914).

- 3:9654 *d,l*-3-CHLORO-2,2,3-TRIMETHYLHEXANE  $\text{C}_9\text{H}_{19}\text{Cl}$  Beil. S.N. 10  
 (*ter*-Butyl-methyl-*n*-propyl-carbinyl  
 chloride)



B.P. 64.2-65.5° at 12.5-13 mm. (1)

(1)

[For prepn. of  $\bar{C}$  from 2,2,3-trimethylhexanol  
 [Beil. I<sub>2</sub>-(458)] (1) by saturation with dry HCl at 0°

3:9654 (1) Petrov, Karasev, Cheltsova, *Bull. soc.* "

- 3:9656 3-CHLORO-2,2-DIMETHYL  
 (*ter*-Butyl-diethyl-carbinyl chloride)



B.P. 53-54° at 6 mm. (1)

[For prepn. of  $\bar{C}$  from 2,2-dimethyl-3-ol  
 (1) with dry HCl gas at 0° see (1).]

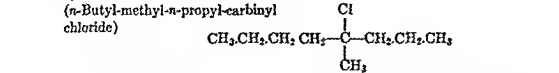
$\bar{C}$  on distn. at 150 mm. loses HCl (1) yielding a

3:9656 (1) Bartlett, Knox, *J. Am. Chem. Soc.* 61,

[For prepn. of  $\tilde{C}$  from 3-methyloctanol-3 (*n*-amyl-ethyl-methyl-carbinol) (1) with HCl gas (72% yield) see (1).]

3:9642 (1) Whitmore, Williams, *J. Am. Chem. Soc.* 55, 408-409 (1933). (2) Smart, Quayle, *J. Am. Chem. Soc.* 67, 21 (1945).

3:9644 *d,l*-4-CHLORO-4-METHYLOCTANE  $C_9H_{19}Cl$  Beil. S.N. 19

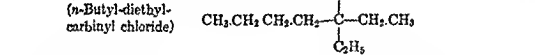


B.P. 70.8-71.4° at 14.5 mm. (1)  $D_4^{25} = 0.8690$  (1)  $n_D^{25} = 1.4338$  (2)  
 $D_4^{20} = 0.8723$  (1)  $n_D^{20} = 1.4300$  (2)  
 1.4349 (1)

[For prepn. of  $\tilde{C}$  from 4-methyloctanol-4 (*n*-butyl-methyl-*n*-propyl-carbinol) [Beil. I-(211)] (1) with dry HCl at -10° see (1).]

3:9644 (1) Whitmore, Woodburn, *J. Am. Chem. Soc.* 55, 363-364 (1933). (2) Smart, Quayle, *J. Am. Chem. Soc.* 67, 21 (1945).

3:9646 *d,l*-3-CHLORO-3-ETHYLHEPTANE  $C_9H_{19}Cl$  Beil. S.N. 19

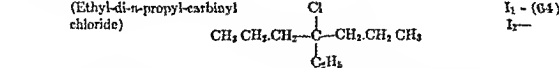


B.P. 46.0° at 3 mm. (1)  $D_4^{25} = 0.8822$  (1)  $D_4^{20} = 0.8856$  (1)  $n_D^{20} = 1.4400$  (1)

[For prepn. of  $\tilde{C}$  from 3-ethylheptanol-3 (*n*-butyl-diethyl-carbinol) [Beil. I-(211), I-(457)] (1) with dry HCl gas at -10° see (1).]

3:9646 (1) Whitmore, Woodburn, *J. Am. Chem. Soc.* 55, 363-364 (1933).

3:9648 4-CHLORO-4-ETHYLHEPTANE  $C_9H_{19}Cl$  Beil. I —



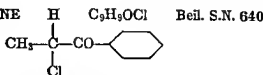
B.P. 67-68° at 12 mm. (1)  $D_4^{20} = 0.8821$  (1)  $n_D^{20} = 1.4438$  (2)  
 92-94° at 10 mm. (2)  $D_4^{16} = 0.884$  (2)  $n_D^{15} = 1.43878$  (1)

[For prepn. of  $\tilde{C}$  from 4-ethylheptanol-4 (ethyl-di-*n*-propyl-carbinol) [Beil. I-424, I-(212), I-(457)] by saturation with HCl gas see (1); for formn. of  $\tilde{C}$  from 3-*n*-propylhexene-2 (2) with conc. HCl see (2).]

[For data on density and parachor of  $\tilde{C}$  at 0°, 15°, 25°, and 65° see (3).]  
 $\tilde{C}$  with  $AlCl_3 + C_6H_6$  gives 67% yield 4-ethyl-4-phenylheptane, b.p. 127-128° at 15 mm.,  $D_4^{20} = 0.8693$ ,  $n_D^{25} = 1.49211$  (1).]

3:9648 (1) Halve, *J. prakt. Chem.* (2) 89, 456-457 (1914) (2) Nasarov, *Ber.* 70, 624 (1937).  
 (3) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* 61, 3197-3111 (1939).

**3:9664  $\alpha$ -CHLOROETHYL PHENYL KETONE**  
( $\alpha$ -Chloropropiophenone)

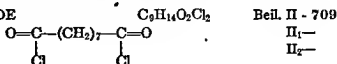


B.P. 131-133° at 26 mm. (1)

[For prepn. (66.4% yield (1)) from  $\alpha$ -chloropropionyl chloride (3:5320) + C<sub>6</sub>H<sub>6</sub> + AlCl<sub>3</sub> see (1).]

3:9664 (1) Baker, Barkenbus, *J. Am. Chem. Soc.* 58, 263 (1936).

**3:9680 AZELAYL (DI)CHLORIDE**



B.P. 180-183° at 35 mm. (1)

166° at 18 mm. (2)

165° at 13 mm. (1)

140° at 0.4 mm. (3)

[For prepn. of  $\bar{\text{C}}$  from azelaic acid (1:0695) with PCl<sub>5</sub> (1) or with SOCl<sub>2</sub> (2) (3) see indic. refs.]

[ $\bar{\text{C}}$  with 1 mole MeOH should yield 8-carbomethoxyoctanoyl chloride-1, b.p. 150-155° at 15 mm. (7), usually prepd. from methyl hydrogen azelate, b.p. 190-195° at 15 mm., m.p. 21-24° (7), with SOCl<sub>2</sub> (7).]

$\bar{\text{C}}$  on htg. with disodium azelate yields (1) azelaic anhydride, m.p. 54-56° (1) (this prod. is probably the linear polymeric  $\alpha$ -anhydride (see 1:0695)).

[ $\bar{\text{C}}$  with C<sub>6</sub>H<sub>6</sub> + AlCl<sub>3</sub> yields (1) 1,9-diphenylnonanedione-1,9, m.p. 44° (1);  $\bar{\text{C}}$  with toluene + AlCl<sub>3</sub> yields (4) 1,9-di-*p*-tolylonanedione-1,9, m.p. 78-79° (4).]

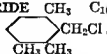
$\bar{\text{C}}$  with phenol yields (5) (6) diphenyl azelate, m.p. 59-60° (6), 49-50° (5).

[ $\bar{\text{C}}$  with MeZnI yields (2) undecanedione-2,10, m.p. 64° (2).]

$\bar{\text{C}}$  on hydrolysis yields azelaic acid (1:0695), m.p. 106° (for the diamide, dianilide, di-*p*-toluidide, and other derivs. corresp. to  $\bar{\text{C}}$  see 1:0695).

3:9680 (1) Etalx, *Ann. chim.* (7) 9, 397-401 (1896). (2) Blaise, Koehler, *Bull. soc. chim.* (4) 5, 692 (1909). (3) Ruzicka, Boekennoogen, *Helv. Chim. Acta* 14, 1332 (1931). (4) Borsche, *Ber.* 52, 2081-2082 (1919). (5) Bouchonnet, *Compt. rend.* 140, 1599 (1905). (6) Marangoni, *Atti. Ist. Veneto sci. Pl. 2, Sci. math. nat.* 97, 209-218 (1937-38); *Cent.* 1939, I 96; *C.A.* 34, 6934-6935 (1940). (7) Morgan, Walton, *J. Chem. Soc.* 1936, 903.

**3:9701 2,3,6-TRIMETHYLBENZYL CHLORIDE**      CH<sub>3</sub>      C<sub>10</sub>H<sub>13</sub>Cl      Beil. S.N. 469



This compound is apparently unreported although the corresp. 2,3,6-trimethylbenzyl bromide, b.p. 146° at 23 mm., 130-132° at 14 mm., has been obtd. (41% yield (1)) from prehnitene (1,2,3,4-tetramethylbenzene) (1:7548) by bromination.

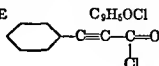
Certain derivatives of  $\bar{\text{C}}$  are, however, recorded here because of the desirability of comparison with the corresp. derivs. of 2,4,5-trimethylbenzyl chloride (3:9702) and of 2,4,6-trimethylbenzyl chloride (3:0372).

— 2,3,6-Trimethylbenzyl alcohol: m.p. 83.5-85° (1).

— 2,3,6-Trimethylbenzyl acetate: oil, b.p. 152° at 23 mm. (1).

3:9701 (1) Smith, Agre, *J. Am. Chem. Soc.* 60, 652-653 (1938).

## 3:9658 PHENYLPROPIOLYL CHLORIDE

Beil. IX - 635  
IX<sub>1</sub>—

B.P. 130-133° at 25-30 mm. (1)

115-116° at 17 mm. (2)

119° at 12 mm. (3)

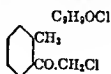
[For prepn. of  $\bar{C}$  from phenylpropiole acid (1:0745) with  $\text{PCl}_5$  (1) (2) cf. (3), or refluxed with 7 pts  $\text{SOCl}_2$  (90-95% yield (4)) (3), or from sodium propiolate (available from pharmaceutical industry (5)) with  $\text{SOCl}_2$  (5) but not  $\text{PCl}_5$  (2), see indic. refs. Note that phenylpropiole acid (1:0745) dislvd. in 2 pts.  $\text{POCl}_3$  at 100° and htd. 3 min. beyond first sepn. of cryst. (6), or the acid refluxed with  $\text{Ac}_2\text{O}$  (7), gives good yield 1-phenylnaphthalene-2,3-dicarboxylic anhydride [Beil. XVII-541, XVII<sub>r</sub>-(275)], ndls. from  $\text{C}_6\text{H}_6$  + lgr., m.p. 255°.]

[For reactn. of  $\bar{C}$  with  $\text{AlCl}_3$  + anisole (1:7445) yielding (1) (3) *p*-methoxyphenyl phenylethynyl ketone [Beil. VIII-199], m.p. 100° (1) (3) (dibromide, ro.p. 138-140° (3)), see indic. refs.; for reactn. of  $\bar{C}$  with  $\text{AlCl}_3$  + methyl *p*-tolyl ether (1:7495) giving (60% yield (5)) 2-hydroxy-5-methyl- $\beta$ -chlorochalcone, deep yel. ndls. from pet. eth., m.p. 95.5° (which in alc. on dropwise treatment with dil. aq.  $\text{NaOH}$  ring-closes by loss of  $\text{HCl}$  to give quant. (5) 6-methylflavone [Beil. XVII<sub>1</sub>-(206)], m.p. 122° (5)), see (5); for reactn. of  $\bar{C}$  with  $\text{AlCl}_3$  + resorcinol (1:1530) in nitrobenzene to give 7-hydroxyflavone [Beil. XVII<sub>1</sub>-58], m.p. 241°, see (8).]

[For reactn. of  $\bar{C}$  with diethyl sodio-malonate (4), ethyl sodio-acetoacetate (4), sodio-acetylacetone (4), with  $\text{Na}$  phenylacetylene or phenyl-ethynyl  $\text{MgBr}$  (9) see indic. refs.]

$\bar{C}$  on hydrolysis (presumably) yields phenylpropiole acid (1:0745), m.p. 130°. For the amide, amide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see the acid (1:0745).

3:9659 (1) Stockhausen, Gattermann, *Ber.* 25, 3537-3538 (1892). (2) Rupe, *Ann.* 369, 329 (1909). (3) Watson, *J. Chem. Soc.* 85, 1324-1325 (1904). (4) Ruhemann, Merriman, *J. Chem. Soc.* 87, 1389-1395 (1905). (5) Simonis, Lear, *Ber.* 59, 2908-2913 (1926). (6) Michael, *Ber.* 39, 1911-1912 (1906). (7) Michael, Bucher, *Am. Chem. J.* 29, 91-92 (1898). (8) Seka, Proschke, *Monatsh.* 69, 289 (1936). (9) Hess, Weltzien, *Ber.* 54, 2515-2516 (1921).

3:9660  $\alpha$ -METHYLPHENACYL CHLORIDE(Chloromethyl  $\alpha$ -tolyl ketone;  
 $\omega$ -chloro- $\alpha$ -methylacetophenone)

Beil. S.N. 640

B.P. 129-130° at 11 mm. (1)

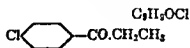
Clear pale yel. liq. (1). — Strong lachrymator!

[For prepn. from benzyl  $\text{MgCl}$  + chloroacetic acid anhydride (3:0730) (42% yield (1)) see (1); from  $\alpha$ -toluyl chloride (3:8740) + diazomethane see (2)]

$\bar{C}$  on oxidn. with  $\text{NaOCl}$  gives (50% yield (1))  $\alpha$ -toluic ac. (1:0690), m.p. 104° (1).

⊙ Chloromethyl  $\alpha$ -tolyl ketone semicarbazone: m.p. 103-105° (1).

3:9660 (1) Austin, Johnson, *J. Am. Chem. Soc.* 54, 656 (1932). (2) Mercer, Robertson, Cahn, *J. Chem. Soc.* 1935, 1000.

—  $\beta$ -CHLOROPHENYL ETHYL  
KETONEBeil. VII - 301  
VII<sub>1</sub>—

B.P. 152° at 30 mm.

M.P. 35-30°

See 3:0310. Division A: Solids.



3:0980 *p*-DICHLOROBENZENE $C_6H_4Cl_2$ 

Beil. V - 203

V<sub>1</sub>-(111)V<sub>2</sub>-(154)

M.P.		B.P.			
55°	(1) (51)	174°	at 764.2 mm.	(24)	$D_4^{50.3} = 1.2189$ (33)
54° (2), cor.	(3)	173.7°	cor.	(5)	$n_D^{80.3} = 1.52104$ (33)
53.3-54.2°	(4)	173.5°	at 755 mm.	(31)	$D_4^{69.9} = 1.2310$ (33)
53.2°	(5) (6) (7)	173.0°		(26) (27)	$n_D^{69.9} = 1.52065$ (33)
53-54°	(8) (57)	172°		(14) (16) (60)	
53.0-53.1°	(24)	171°		(15)	
53°	(9) (10) (11)	170-171° u.c.		(32)	
	(12) (13) (14)				
	(15) (16) (49)				
	(50) (60)				
52.9°	(17) (18) (19)				
	(20) (21)				
52.84°	(22)				
52.8°	(23)				
52.72°	(25)				
52.70°	(30)				
52.69°	(26)				
52.0°	(27)				
52.62°	(28)				
52.0°	(31)				
52-53°	(29)				

Colorless cryst., alm. insol. aq. (0.077 g. per 1000 g. aq. at 30° (22) cf. (13)); misc. hot alc. (50 ml. abs. alc. + 5 ml. aq. at 25° dis. 4.55 g.  $\bar{C}$  (26)), eas. sol. ether,  $C_6H_6$ ,  $CHCl_3$ ,  $CS_2$ . — Readily sublimes; eas. volatile with steam.

[For data on crystallographic consts. see (34) (35); for data on rate of evapn. of cryst.  $\bar{C}$  see (11);  $\bar{C}$  has molec. f.p. depression of 77 (36) and because of its accessibility, ease of purification, convenient m.p. and large f.p. depression is often used for making mol. wt. detns.]

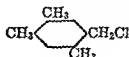
[For f.p./compn. data and diagram of system  $\bar{C}$  + *o*-dichlorobenzene (3:6055) (eutectic, m.p. -23.4° contg. 13.3%  $\bar{C}$ ) see (17) (27); for f.p./compn. data and diagram for system  $\bar{C}$  + *m*-dichlorobenzene (3:5960) (eutectic, m.p. -29.9° contg. 12.0%  $\bar{C}$ ) see (17); for f.p./compn. data on ternary system of all three dichlorobenzenes see (27). — For f.p./compn. data and diagrams for systems  $\bar{C}$  + biphenyl (1:7175) (eutectic, m.p. 26.9° contg. 57.5 mole %  $\bar{C}$  (6)) (19),  $\bar{C}$  + naphthalene (1:7200) (eutectic, m.p. 30.2° contg. 60.6 mole %  $\bar{C}$  (6)),  $\bar{C}$  + triphenylmethane (1:7220) (eutectic, m.p. 35.9° contg. 68.5 mole %  $\bar{C}$  (6)),  $\bar{C}$  + nitrobenzene (eutectic, m.p. -6.8° contg. 32%  $\bar{C}$  (9)),  $\bar{C}$  + *p*-chlorophenol (3:0475) (eutectic, m.p. 27.2° contg. 26.6 mole %  $\bar{C}$  (18)) see indic. refs. — For thermal anal. of system  $\bar{C}$  +  $SbCl_3$  (eutectic, m.p. 39.5° contg. 49.5 wt. %  $\bar{C}$  (37)), and of system  $\bar{C}$  +  $SbBr_3$  (eutectic, m.p. 48.5° contg. 73.5 wt. %  $\bar{C}$  (37)), see (37).]

[ $\bar{C}$  with *p*-dibromobenzene gives a series of solid solns. cf. (38) (39) (40) (41) (23) (24) (26); for study of systems  $\bar{C}$  + *p*-chloro-iodobenzene (23) (34) and  $\bar{C}$  + *p*-di-iodobenzene (23) see indic. refs.]

[For data on densities of solns. of  $\bar{C}$  in  $C_6H_6$  (1:6400) and in *n*-hexane (1:8530) see (42); for data on  $D_4^{25}$  and  $n_D^{25}$  of solns. of  $\bar{C}$  in  $C_6H_6$  see (7).]

3:9702 2,4,5-TRIMETHYLBENZYL CHLORIDE  
(*ω*-Chlorodurene) $C_{10}H_{13}Cl$ 

Beil. V —

 $V_1$  — $V_2$  - (329)

B.P. 130° at 15 mm. (1)  
 111-116° at 6 mm. (2)  
 110° at 5 mm. (2)  
 98-108° at 1 mm. (3)

[See also the isomeric 2,4,6-trimethylbenzyl chloride (3:0372).]

[For prepn. of  $\bar{C}$  from 1,2,4-trimethylbenzene (pseudocumene) (1:7470) by chloromethylation with formalin (1:0145) + conc. HCl + HCl gas (yields: 70% (2), 40-43% (3)), or with paraformaldehyde + HCl +  $ZnCl_2$  (4), or with chloromethyl methyl ether (3:7085) in AcOH without cat. (yields. 60% (1), 50-60% (5)) (note that some bis (chloromethylated) product is also formed) see indic. refs; for prepn. of  $\bar{C}$  from 2,4,5-trimethylbenzyl alc. (see below) with conc. HCl under reflux 5 hrs see (2).]

[ $\bar{C}$  on catalytic hydrogenation presumably yields 1,2,4-trimethylbenzene (pseudocumene) (1:7470) although this particular reaction is not actually reported cf. (1).]

[ $\bar{C}$  on hydrolysis presumably yields 2,4,5-trimethylbenzyl alcohol, cryst from alc., m.p. 83.0-83.5° (2); note, however that this reaction is not actually reported, the alc. having been obtd. by hydrolysis of its acetate, oil, b.p. 141-150° at 9 mm. (2).]

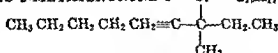
$\bar{C}$  in alc. with aq. NaCN refluxed 5 hrs. gives (85% yield (2)) 2,4,5-trimethylbenzyl cyanide, m.p. 9-10°, b.p. 133-147° at 4 mm. (2); note that this nitrile upon hydrolysis with 50%  $H_2SO_4$  at 100° for 2½ hrs. gives 2,4,5-trimethylphenylacetic acid, crude m.p. 116-118° (2), pure m.p. 128-129° (2) (corresp. dinitro deriv., m.p. 203-203.5° (2)).

[For condensation of  $\bar{C}$  with ethyl sodio-acetoacetate see (3).]

3:9703 (1) Vavon, Bolle, Calin, *Bull. soc. chim.* (5) 6, 1025-1033 (1930) (2) Smith, MacMullen, *J. Am. Chem. Soc.* 58, 633-635 (1936) (3) John, Gunther, *Ber.* 74, 887-888 (1941). (4) Bert, *Comp. rend.* 186, 373-374 (1928) (5) Vavon, Bolle, *Comp. rend.* 204, 1826-1828 (1937).

3:9710 *d,l*-3-CHLORO-3-METHYLNONYNE-4 $C_{10}H_{17}Cl$ 

Beil. S.N. 12



B.P. 82° at 17 mm. (1)

 $D_4^{20} = 0.8068$  (1) $n_D^{20} = 1.4543$  (1)

[For prepn. of  $\bar{C}$  from 3-methylnonyn-4-ol-3 (1) by saturation with HCl gas (72% yield) see (1).]

[ $\bar{C}$  with MeMgBr gives 73% yield 3,3-dimethylnonyne-4, b.p. 82° at 40 mm,  $D_4^{20} = 0.7658$ ,  $n_D^{20} = 1.4313$  (1).]

3:9710 (1) Campbell, Eby, *J. Am. Chem. Soc.* 62, 1799-1800 (1940).

## 3:0712 5-CHLORODECENE-5

Cl

 $C_{10}H_{19}Cl$ 

Beil. S.N. 11



B.P. 99-100° at 28 mm. (1)

 $D_4^{25} = 0.8753$  (1) $n_D^{25} = 1.4448$  (1)

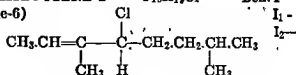
Two from stereoisomers of  $\bar{C}$  are possible, but only this one has as yet been recognized.

[For prepn. of  $\bar{C}$  from decyne-5 (di-*n*-butylacetylene) [Beil. I<sub>2</sub>-(230)] with AcCl +  $SnCl_4$

(4-chloro-3-*n*-butylocten-3-one-2, b.p. 140-146° at 28 mm.;  $D_4^{25} = 0.9459$ ,  $n_D^{25} = 1.4612$ , is also formed (1)) see (1).]

3:9712 (1) Kroeger, Sowa, Nieuwland, *J. Org. Chem.* 1, 163-169 (1936).

3:9714 *d,l*-4-CHLORO-3,7-DIMETHYLOCTENE-2  $C_{10}H_{19}Cl$  Beil. I—  
(5-Chloro-2,6-dimethyloctene-6)  $I_1 - (96)$

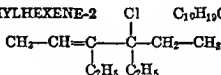


B.P. 83-84° at 12 mm. (1)

[For prepn. of  $\bar{C}$  from 2,6-dimethylocten-6-ol-5 [Beil. I-452,  $I_1-(232)$ ] with 6 *N* HCl see (1).]

3:9714 (1) Abelman, *Ber.* 43, 1583 (1910).

3:9716 4-CHLORO-3,4-DIETHYLHEXENE-2  $C_{10}H_{19}Cl$  Beil. S.N. 11



B.P. 70-72° at 10 mm. (1)  $D_4^{19} = 0.807$  (1)  $n_D^{15} = 1.4551$  (1)

For prepn. of  $\bar{C}$  from 3,4-diethylhexene-3 (1) with  $\text{Cl}_2 + \text{NaHCO}_3$  at 0° (60% yield accompanied by 40% yield of 3,4-dichloro-3,4-diethylhexane (3:9724)) see (1).]

$\bar{C}$  on treatment with  $\text{O}_3$  yields (1) acetaldehyde (1:0100) q.v.

3:9710 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1233-1246 (1938); *Cent.* 1939, II 4222; *C.A.* 33, 4190 (1939).

3:9720 1,10-DICHLORODECANE  $C_{10}H_{20}Cl_2$  Beil. S.N. 10  
(Decamethylene (di)chloride)



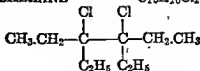
B.P. 147-148° at 11 mm. (1)  $D_4^{22} = 0.9941$  (1)

[For prepn. of  $\bar{C}$  from decanediol-1,10 (decamethylene glycol) (1:5961) by htg. 1 day with excess  $\text{SOCl}_2$  see (1).]

$\bar{C}$  with NaI in acetone refluxed 4 hrs., acetone evaporated, residual material htd. for 3 hrs. at 140-160° with thiourea in isoamyl alc., yields (1) decamethylene  $\omega,\omega'$ -bis-(isothioureahydrochloride), m.p. 186° (1).

3:9720 (1) Kawai, Hosono, Shikunami, Yonechi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* 16, Nos. 306-309, 9-16 (1931); *Cent.* 1931, II 1694; *C.A.* 25, 5665 (1931).

3:0724 3,4-DICHLORO-3,4-DIETHYLHEXANE  $C_{10}H_{20}Cl_2$  Beil. S.N. 10



B.P. 101-103 at 10 mm. (1)

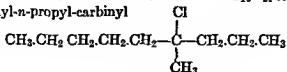
$D_4^{19} = 1.022$  (1)  $n_D^{15} = 1.47485$  (1)

[For prepn. of  $\bar{C}$  from 3,4-diethylhexene-3 (1) with  $\text{Cl}_2 + \text{NaHCO}_3$  at  $0^\circ$  (yield 40% accompanied by 60% 4-chloro-3,4-diethylhexene-2 (3:9716)) see (1).]

3:9724 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, II 4222; *C.A.* 33, 4190 (1939).

3:9739 *d,l*-4-CHLORO-4-METHYLNONANE  $\text{C}_{10}\text{H}_{21}\text{Cl}$  Beil. S.N. 19

(*n*-Amyl-methyl-*n*-propyl-carbinyl chloride)



B.P.  $43-45^\circ$  at 1 mm. (1)

$D_4^{25} = 0.8663$  (1)

$n_D^{25} = 1.4369$  (2)

$n_D^{20} = 1.4389$  (2)

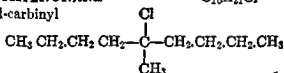
1.4375 (1)

[For prepn. of  $\bar{C}$  from 4-methylnonanol-4 (*n*-amyl-methyl-*n*-propyl-carbinol) (1) with  $\text{HCl}$  gas (85% yield (1)) see (1).]

3:9730 (1) Whitmore, Williams, *J. Am. Chem. Soc.* 55, 408-409 (1933). (2) Smart, Quayle, *J. Am. Chem. Soc.* 67, 21 (1945).

3:0732 5-CHLORO-5-METHYLNONANE  $\text{C}_{10}\text{H}_{21}\text{Cl}$  Beil. S.N. 10

(*Di-n*-butyl-methyl-carbinyl chloride)



B.P.  $75-77^\circ$  at 10 mm. (3)

$D_4^{25} = 0.8676$  (1)

$60.5^\circ$  at 3.5 mm. (1)

$D_4^{20} = 0.8707$  (1)  $n_D^{20} = 1.4382$  (1)

[For prepn. of  $\bar{C}$  from 5-methylnonanol-5 (*di-n*-butyl-methyl-carbinol) (Beil. I-213), I-460] (1) by saturation with dry  $\text{HCl}$  gas at  $-10^\circ$  see (1) ]

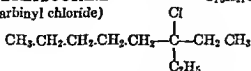
$\bar{C}$  on refluxing with  $2\frac{1}{2}$  pts. aq. for 9 hrs. gives 14% of its halogen as halide ion (1) (the resultant olefin was not isolated).

[For behavior of  $\bar{C}$  with naphthalene +  $\text{AlCl}_3$  in  $\text{CS}_2$  see (3).]

3:9732 (1) Whitmore, Woodburn, *J. Am. Chem. Soc.* 55, 363-364 (1933). (2) Woodburn, Whitmore, *J. Am. Chem. Soc.* 56, 1394-1395 (1934). (3) Petrov, Kurbskii, *J. Gen. Chem. (U.S.S.R.)* 14, 492-494 (1944); *C.A.* 39, 4600 (1945).

3:9734 *d,l*-3-CHLORO-3-ETHYLOCTANE  $\text{C}_{10}\text{H}_{21}\text{Cl}$  Beil. S.N. 10

(*n*-Amyl-diethyl-carbinyl chloride)



B.P.  $42-43^\circ$  at 0.5 mm. (1)

$D_4^{25} = 0.8792$  (1)

$n_D^{20} = 1.4423$  (1)

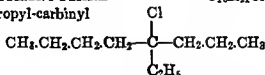
[For prepn. of  $\bar{C}$  from 3-ethyloctanol-3 (*n*-amyl-diethyl-carbinol) (Beil. I-426) (1) with  $\text{HCl}$  gas (72% yield (1)) see (1).]

3:9734 (1) Whitmore, Williams, *J. Am. Chem. Soc.* 55, 408-409 (1933).

- 3:9736 *d,l*-4-CHLORO-4-ETHYLOCTANE  
(*n*-Butyl-ethyl-*n*-propyl-carbinyl  
chloride)

 $C_{10}H_{21}Cl$ 

Beil. S.N. 10



B.P. 53-54° at 2 mm. (1)

 $D_4^{25} = 0.8773$  (1) $D_4^{20} = 0.8804$  (1)  $n_D^{20} = 1.4421$  (1)

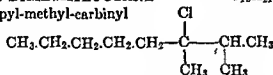
[For prepn. of  $\bar{C}$  from 4-ethyloctanol-4 (*n*-butyl-ethyl-*n*-propyl-carbinol) [Beil. I<sub>2</sub>-(460)] (1) by saturation with dry HCl gas at -10° see (1).]

- 3:9736 (1) Whitmore, Woodburn, *J. Am. Chem. Soc.* 55, 363-364 (1933).

- 3:9738 3-CHLORO-2,3-DIMETHYLOCTANE  
(*n*-Amyl-isopropyl-methyl-carbinyl  
chloride)

 $C_{10}H_{21}Cl$ 

Beil. S.N. 10



B.P. 53-55° at 3 mm. (1)

 $D_4^{20} = 0.8818$  (1) $n_D^{20} = 1.4420$  (1)

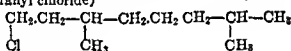
[For prepn. of  $\bar{C}$  from 2,3-dimethyloctanol-3 (1) with dry HCl gas at 0° (77% yield) see (1).]

- 3:9738 (1) Whitmore, Evers, *J. Am. Chem. Soc.* 55, 813-814 (1933).

- 3:9740 8-CHLORO-2,6-DIMETHYLOCTANE  
(Tetrahydrogeranyl chloride;  
perhydrogeranyl chloride)

 $C_{10}H_{21}Cl$ 

Beil. I -

I<sub>1</sub> - (65)I<sub>2</sub> -

B.P. 88-80° at 12 mm. (1)

85-86° at 10 mm. (2)

[For prepn. of  $\bar{C}$  from 2,6-dimethyloctanol-8 [Beil. I-426, I<sub>1</sub>-(214), I<sub>2</sub>-(461)] (1) with dry HCl (1) or with  $PCl_5$  (2) see indic. refs.]

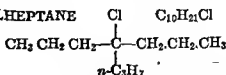
[For conversion of  $\bar{C}$  to common  $\bar{C}$  of latter with chloromethyl methyl ether (3:7085) to 8-dimethylnonane, b.p. 94-94.5° at 14.5 mm.,  $n_D^{20} =$

- 3:9740 (1) Smith, Ungnade, Austin, Prichard, Opie, *J. Org. Chem.* 4, 338-340 (1939). (2) Ishizaka, *Ber.* 47, 2454 (1914).

- 3:9742 4-CHLORO-4-*n*-PROPYLHEPTANE  
(Tri-*n*-propylcarbinyl  
chloride)

 $C_{10}H_{21}Cl$ 

Beil. I -

I<sub>1</sub> - (66)I<sub>2</sub> -

B.P. 80° at 12 mm. (1)

 $D_4^{20} = 0.8779$  (1)  $n_D^{15} = 1.44209$  (1)

[For prepn. of  $\bar{C}$  from 4-*n*-propylheptanol-4 [Beil. I-426, I<sub>1</sub>-(214), I<sub>2</sub>-(461)] by saturation with dry HCl see (1).]

1335

## LIQUIDS (WITH B.P. REPTD. AT RED. PRESS.)

3:9742-3:9750

[For data on density and parachor of  $\bar{C}$  at 0°, 15°, 25°, 50°, and 75° see (2).]  
 [For reactn. of  $\bar{C}$  with  $AlCl_3$  +  $C_6H_6$  yielding 4-phenyl-4-n-propylheptane, b.p. 140-141° at 15 mm.,  $D_4^{20} = 0.8694$ ,  $n_D^{15} = 1.4924$ , see (1)]

3:9742 (1) Halse, *J. prakt. Chem.* (2) 89, 459 (1914). (2) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* 61, 3107-3111 (1939).

3:9744 4-CHLORO-2,4,6-TRIMETHYLHEPTANE  
 (Di-isobutyl-methyl-carbinyl  
 chloride)

B.P. 82-83° at 25 mm. (1)

[For prepn. of  $\bar{C}$  from 2,4,6-trimethylheptanol-4 (di-isobutyl-methyl-carbinol) [Beil. I-127, I-1(215)] (1) by saturation with dry HCl gas see (1)]  
 [For reactn. of  $\bar{C}$  with  $AlCl_3$  +  $C_6H_6$  to give 4-phenyl-2,4,6-trimethylheptane, b.p. 143-144° at 18 mm.,  $D_4^{20} = 0.8753$ ,  $n_D^{15} = 1.49497$  see (1).]

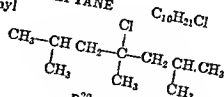
3:9744 (1) Halse, *J. prakt. Chem.* (2) 89, 453-459 (1914).

3:9750 2,4,6-TRIMETHYLBENZOYL CHLORIDE  
 (Mesitoyl chloride;  
 $\beta$ -isodurylyl chloride)

B.P. 143-146° at 60 mm. (1)  
 118-119° at 19 mm. (2)  
 115.5-116.5° at 18 mm. (3)  
 85.0-85.5° at 4 mm. (4)  
 85.5-86.5° at 2-3 mm. (5)

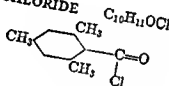
[For prepn. of  $\bar{C}$  from 2,4,6-trimethylbenzoic acid (mesitoic acid) [Beil. IX-553, IX-1(214)] (1) with  $SOCl_2$  (90-97% yield (1)) (2) (3) (5) (6) see indic. refs]  
 [ $\bar{C}$  with MeOH yields (3) (4) methyl-2,4,6-trimethylbenzoate (mesitoate) [Beil. IX-553], b.p. 212°, 102-103° at 5 mm. (3), 101-102° at 3 mm.,  $n_D^{20} = 1.4970$  (4)]  
 [ $\bar{C}$  with 2,4,6-trimethylphenyl MgBr yields (5) (6) 2,4,6,2',4',6'-hexamethylbenzophenone (dimesityl ketone), m.p. 138-139° (5), 136-137° (6);  $\bar{C}$  with 2,4,6-trimethylphenacyl MgBr gives (7) 2,4,6,2',4',6'-hexamethyldibenzoylmethane (dimesitylmethane), m.p. 96-97° (7)]  
 [ $\bar{C}$  on hydrolysis yields (4) 2,4,6-trimethylbenzoic acid, m.p. 152° (amide, m.p. 189° (9), 188-188.5° (1), 187-188° (8)).]

3:9750 (1) Barnes, *Org. Syntheses* 21, 77-79 (1941). (2) Murray, Cleveland, Saunders, *J. Am. Chem. Soc.* 63, 3121 (1941). (3) Kadewsch, Weller, *J. Am. Chem. Soc.* 63, 1311 (1941). (4) Norris, Young, *J. Am. Chem. Soc.* 57, 1421 (1935). (5) Nauta, Wuis, *Rec. trav. chim.* 56, 537-538 (1937). (6) Kohler, *Baltzly, J. Am. Chem. Soc.* 54, 4023 (1932). (7) Fuson, Fugate, Fisher, *J. Am. Chem. Soc.* 61, 2363 (1939). (8) Wheeler, *Am. Chem. J.* 23, 468 (1900). (9) Hantzsch, Lucas, *Ber.* 28, 745 (1895).



Beil. I -  
 I-1 - (66)  
 I-2 -

$D_4^{20} = 0.8657$  (1)  $n_D^{15} = 1.43336$  (1)

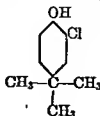


Beil. S.N. 943

$D_4^{25} = 1.0967$  (3)  $n_D^{25} = 1.5263$  (3)

3:9760 2-CHLORO-4-*ter*-BUTYLPHENOL $C_{10}H_{13}OCl$ 

Beil. S.N. 530-2



B.P. 113-115° at 8 mm. (1)

85-86° at 3-4 mm. (2)

84.5-85° at 3-4 mm. (3)

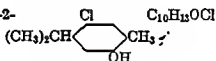
[For prepn. of  $\bar{C}$  from *p-ter*-butylphenol (1:1510) by chlorination with *N*-chloroacetamide (cf. (4) (5)) see (1); for other methods see (2) (3).]

[For study of mercuration of  $\bar{C}$  see (6).]

⑨ 4-*ter*-Butyl-2-chlorophenyl *p*-nitrobenzyl ether: colorless pl. from EtOH, m.p. 90° (1).

3:9760 (1) Jones, *J. Chem. Soc.* 1942, 678. (2) Mills (to Dow Chem. Co.), U.S. 2,176,010, Oct. 10, 1939; *C. A.* 34, 858 (1940). (3) Mills (to Dow Chem. Co.), U.S. 2,221,807, Nov. 19, 1940; *C. A.* 35, 1936 (1941). (4) Orton, King, *J. Chem. Soc.* 99, 1185-1192 (1911). (5) Orton, Bradfield, *J. Chem. Soc.* 1927, 993. (6) Moness, Christiansen (to E. R. Squibb), U.S. 2,137,236, Nov. 22, 1938; *Cent.* 1939, I 5007; *C. A.* 33, 1885-1886 (1939).

## — 4-CHLORO-5-ISOPROPYL-2-METHYLPHENOL

 $C_{10}H_{13}OCl$ 

Beil. S.N. 531

B.P. 158° at 52 mm.

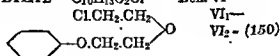
M.P. 42-43°

See 3:0480. Division A: Solids.

3:9770  $\beta$ -CHLOROETHYL- $\beta'$ -PHENOXYETHYL ETHER $C_{10}H_{13}O_2Cl$ 

Beil. VI —

[ $\beta$ -( $\beta$ -Phenoxyethoxy)ethyl chloride]



VI1—

VI2— (150)

B.P. 149° at 10 mm. (1)

138-143° at 8 mm. (2)

113-120° at 1 mm. (3)

 $D_{15}^{25} = 1.149$  (1)

[For prepn. (60% yield (1)) from  $\beta,\beta'$ -dichlorodiethyl ether (3:6025) with alc.  $NaOC_2H_5$  (1 mole) see (1).]

[For reaction of  $\bar{C}$  in  $CS_2$  or  $C_6H_6$  with  $AlCl_3$  + phthalic anhydride, succinic anhydride, maleic anhydride, acetic anhydride see (4).]

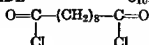
[For condensation with amines and phenols see (5); for use as plasticizer see (6).]

3:9770 (1) Cretcher, Koch, Pittenger, *J. Am. Chem. Soc.* 47, 1174 (1925). (2) Eastman Organic Chemicals, List No. 33 (1942). (3) Bruson (to Röhm and Haas Co.), U.S. 2,249,111, July 15, 1941; *C. A.* 35, 6698 (1941). (4) Bruson, Es Röhm and Haas Co., French 824,857, Feb. 1 (6) Murray, Kenyon (to Eastman Kodak Co. *C. A.* 28, 2532 (1934).

## 3:9780 SEBACYL (DI)CHLORIDE

 $C_{10}H_{18}O_2Cl_2$ 

Beil. II - 719

II<sub>1</sub>-(293)II<sub>2</sub>-(610)

B.P. 220°	at 75 mm. (1)
203°	at 30 mm. (2)
182°	at 16 mm. (3)
168-170°	at 16 mm. (4)
152°	at 15 mm. (5)
162-167°	at 11 mm. (6)
155-156°	at 8 mm. (7)
109-110°	at 1-2 mm. (11)

$$D_4^{20} = 1.1212 \text{ (6)} \quad n_D^{18.3} = 1.46836 \text{ (4)}$$

$$D_4^{25} = 1.1375 \text{ (6)}$$

[For prepn. of  $\bar{C}$  from sebacic acid (1:0730) with  $PCl_5$  (90-95% yield (5) (2) (4), with  $PCl_3$  (3), with  $SOCl_2$  (yield: 100% (1), 86% (6), 84% (7)) (8), 83% (11), or with  $SiCl_4$  in  $C_6H_6$  + ether (37% yield (9)) see indic. refs.]

$\bar{C}$  with MeOH (1 mole) followed by  $Na_2CO_3$  yields (1) methyl hydrogen sebacate, m.p. 36° (1);  $\bar{C}$  with abs. EtOH (1 mole) yields (7) 9-carbethoxynonanoyl chloride ( $C_2H_5OOC.(CH_2)_8.CO.Cl$ ), b.p. 158-160° at 7 mm. (7) (corresp. 9-carbethoxynonanoyl anilide, m.p. 60-61° (7));  $\bar{C}$  with excess phenol yields (8) diphenyl sebacate, m.p. 65-66° (8).

[ $\bar{C}$  with  $AlCl_3 + C_6H_6$  (1:7400) gives (50% yield (2) (4) 1,8-dibenzoyloctane, m.p. 91-92° (4), 88-89° (2);  $\bar{C}$  with  $AlCl_3 + m$ -xylene (1:7420) gives (10) 1,8-bis-(2,4-dimethylbenzoyl)octane.]

[ $\bar{C}$  with  $n$ - $C_8H_{17}MgBr$  gives (28% yield (7)) 10-ketopalmitic acid, m.p. 75-75.8° (7);  $\bar{C}$  with  $n$ - $C_8H_{17}MgBr$  gives (12% yield (7)) 10-ketostearic acid, m.p. 82-82.8° (7);  $\bar{C}$  with  $AgNCO$  yields (11) sebacyl di-isocyanate.

[ $\bar{C}$  in xylene on cat. hydrogenation over  $Pd/CaCO_3$  (6) or  $Pd$ /diatomaceous earth (5) gives (30-40% yield (5)) corresp. dialdehyde, decandial-1,10 [Beil. I<sub>2</sub>-(849)].]

$\bar{C}$  on hydrolysis yields sebacic acid (1:0730); for the diamide, dianilide, di-*p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see 1:0730.

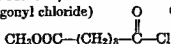
3:9780 (1) Meyer, *Monatsh.* **22**, 421 (1901). (2) Auger, *Ann. chim.* (6) **22**, 361-364 (1891). (3) Borsche, Wollemann, *Ber.* **44**, 3185-3186 (1911). (4) von Auwers, Schmidt, *Ber.* **46**, 480 (1913). (5) Rosenmund, Zetsche, *Ber.* **55**, 609-612 (1922). (6) Waser, *Helv. Chim. Acta* **8**, 124-125 (1925). (7) Fordyce, Johnson, *J. Am. Chem. Soc.* **55**, 3369-3370 (1933). (8) Marangoni, *Atti Ist. Veneto sci. Pl. 2. Sci. mat. nat.* **97**, 209-218 (1937-1938); *Cent.* **1939**, I 96; *C.A.* **34**, 6934-6935 (1940). (9) Montonna, *J. Am. Chem. Soc.* **49**, 2115 (1927). (10) Borsche, *Ber.* **52**, 2078, 2082 (1919).

(11) Lieser, Macura, *Ann.* **548**, 226-254 (1941); *Cent.* **1942**, II 146-148; *C.A.* **37**, 4699 (1942).

3:9792 METHYL  $\omega$ -(CHLOROFORMYL)PELARGONATE

Beil. S.N. 178

( $\omega$ -(Carbomethoxy)pelargonyl chloride)



B.P. 177°	at 23 mm. (1)
158-160°	at 10 mm. (2)

Note that  $\bar{C}$  is both an acid chloride and an ester.

[For prepn. of  $\bar{C}$  from methyl hydrogen sebacate (itself obtd. (52-61% (2)) from sebacic acid (1:0730) + MeOH (1:6120)) by action of  $SOCl_2$  (yields: 83-86% (2), 60-70% (1)) see indic. refs.]



⑤  $\omega$ -(Carbomethoxy)pelargonamide (methyl sebacamate): cryst. from aq., m.p. 77.4° (3), 72-74° (2). [From  $\bar{C}$  with conc. aq.  $\text{NH}_4\text{OH}$  at 8° (yields: 93-95% (2), 90% (3)); for dehydration of this prod. (64-71% yield) (3) with  $\text{P}_2\text{O}_5$  in acetylene tetrachloride to methyl  $\omega$ -cyanopelargonate, b.p. 170° at 14 mm.,  $n_D^{25} = 1.4398$  (3), and use of latter in prepn. of high-mol.-wt. linear polymers (4), see indic. refs.]

3:9792 (1) Morgan, Walton, *J. Chem. Soc.* 1936, 904. (2) Bishop, *Org. Syntheses* 25, 71-72 (1945). (3) Biggs, Bishop, *J. Am. Chem. Soc.* 63, 944 (1941). (4) Bishop (to Bell Telephone Laboratories, Inc.), U.S. 2,277,033, March 24, 1942; *C.A.* 36, 4636 (1942).

3:9800 *n*-UNDECANOYL CHLORIDE  $\cdot \text{C}_{10}\text{H}_{21}\text{OCl}$  Beil. S.N. 162  
(*n*-Hendecanoyl chloride)  $\text{CH}_3(\text{CH}_2)_9\text{C}=\text{O}$



B.P. 119-120° at 40 mm. (1)  
123° at 11 mm. (2)  
90° at 1 mm. (3)

$n_D^{25} = 1.4465$  (3)

Care must be taken to avoid confusion of  $\bar{C}$  with *n*-undecyl chloride (1-chloroundecane) (3:8803).

[For prepn. of  $\bar{C}$  from *n*-undecylic acid (1:0573) with  $\text{SOCl}_2$  (yield: 95.5% (1)) (3) (4) see indic. refs.]

[ $\bar{C}$  with  $\text{C}_6\text{H}_6 + \text{AlCl}_3$  should give *n*-undecyl phenyl ketone, but this compd. is unreported in the literature. —  $\bar{C}$  with toluene (1:7405) +  $\text{AlCl}_3$  gives (80% yield (5)) *n*-undecyl *p*-tolyl ketone, m.p. 32°, b.p. 196-197° at 12 mm. (7)]

[ $\bar{C}$  with MeOH presumably gives methyl *n*-undecylate [Beil. II<sub>1</sub>-(154), II<sub>2</sub>-(314)], b.p. 123° at 9-10 mm. (6); similarly,  $\bar{C}$  with EtOH presumably gives ethyl *n*-undecylate [Beil. II-358, II<sub>1</sub>-(154)] (known in polymorphic forms for which see (7) (8) (9)); note, however, that prepn. of these esters by this means is not actually reported in the literature.]

[ $\bar{C}$  with phenol presumably gives phenyl *n*-undecylate, but neither this cpd. nor either of the *n*-undecyl hydroxyphenyl ketones to be expected from its rearr. with  $\text{AlCl}_3$  is reported in the literature. — However, for reaction of  $\bar{C}$  with hydroquinone (1:1590) see (19).]

[ $\bar{C}$  with sodium undecylate on htg. presumably gives undecylic anhydride, m.p. 36.7° (11), 35° (12), but this cpd. is actually reported only by other methods (11) (12).]

[For reaction of  $\bar{C}$  with diethyl sodioacetosuccinate [Beil. III-801, III<sub>1</sub>-(280), III<sub>2</sub>-(486)] and subsequent hydrolysis of prod. to  $\gamma$ -ketomyristic acid see (4).]

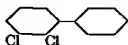
[ $\bar{C}$  with vanillylamine (4-hydroxy-3-methoxybenzylamine) gives (2) cf. (13) *N*-(vanillyl)-myristamide,  $\alpha$ -form, m.p. 69.5° (2);  $\beta$ -form, m.p. 62.0-62.5° (2); the m.p. of 54-56° reported earlier (13) may have been a mixture, but that of 73-74° by other workers (14) is unexplained.]

$\bar{C}$  on hydrolysis yields undecylic acid (1:0573), m.p. 29.3°; for the amide, anilide, *p*-toluidide, and other derivatives corresp. to  $\bar{C}$  see undecylic acid (1:0573).

3:9800 (1) Fierz-David, Kuster, *Helv. Chim. Acta* 22, 86-89 (1939). (2) Ford-Moore, Phillips, *Rec. trav. chim.* 53, 856 (1934). (3) Haskelberg, Bergmann, *J. Soc. Chem. Ind.* 60, 166-168 (1941). (4) Robinson, *J. Chem. Soc.* 1930, 747-748. (5) Hasan, Stedman, *J. Chem. Soc.* 1931, 2120. (6) Lesser, Weiss, *Ber.* 47, 2519 (1914). (7) van Bellinghen, *Bull. soc. chim. Belg.* 47, 647, 659, 673, 674, 676, 677, (1938). (8) Mumford, Phillips, *Rec. trav. chim.* 52, 181-194 (1933). (9) Meyer, Reed, *J. Am. Chem. Soc.* 55, 1552 (1933). (10) Asano, Hase, *J. Pharm. Soc. Japan* 60, 650-659 (1940); 61, 1-6 (1941); *C.A.* 36, 82 (1942).

(11) Wallace, Copenhaver, *J. Am. Chem. Soc.* 63, 699 (1941). (12) Backer, van der Baan, *Rec. trav. chim.* 56, 1166 (1937). (13) Nelson, *J. Am. Chem. Soc.* 41, 2125-2126 (1919). (14) Kobayashi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* 6, 166-184 (1927), *Cent.* 1928, 1 1029.

## 3:9850 2,3-DICHLOROBIPHENYL

 $C_{12}H_8Cl_2$ 

Beil. S.N. 479

B.P. 172° at 30 mm. (1)

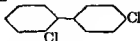
170-176° at 19 mm. (2)

[For prepn. from 2-amino-3-chlorobiphenyl via diazo reactn see (1); for other methods see (2).]

$\bar{C}$  on oxidn. with  $CrO_3 + AcOH$  yields (1) 2,3-dichlorobenzoic acid (3:4550), m.p. 160° (1).

3:9850 (1) de Crauw, *Rec. trav. chim.* 50, 776-777 (1931) (2) Zerweek, Schutz (to General Aniline and Film Corp.), U.S. 2,280,504, April 21, 1942, *C.A.* 36, 5658 (1942).

## — 2,4'-DICHLOROBIPHENYL

 $C_{12}H_8Cl_2$ 

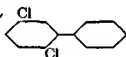
Beil. S.N. 479

B.P. 191° at 30 mm.

M.P. 46°

See 3:0670. Division A: Solids.

## 3:9854 2,5-DICHLOROBIPHENYL

 $C_{12}H_8Cl_2$ 

Beil. V —

V<sub>1</sub>—V<sub>2</sub>-(483)

B.P. 182° at 30 mm. (1)

171° at 15 mm. (2)

147-148° at 8 mm. (3)

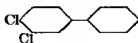
[For prepn of  $\bar{C}$  from 2-amino-5-chlorobiphenyl (1) (2), 4,4'-diamino-2,5-dichlorobiphenyl (20% yield (1)), or 2,5-dichloroaniline (3) via appropriate diazo reactions see (1) (2) (3)]

$\bar{C}$  on oxidn. with  $CrO_3 + AcOH$  yields (1) (2) 2,5-dichlorobenzoic acid (3:4340), m.p. 152° (1), 154° (2).

[For study of reaction of  $\bar{C}$  with NaOMe see (4).]

3:9854 (1) de Crauw, *Rec. trav. chim.* 50, 776-777 (1931). (2) Scarborough, Waters, *J. Chem. Soc.* 1927, 94 (3) I G., French 851,131, Jan 3, 1940, *C.A.* 36, 1950 (1942). (4) Ref. 1, pp. 784-785, 789.

## — 3,4-DICHLOROBIPHENYL

 $C_{12}H_8Cl_2$ 

Beil. V —

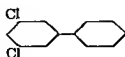
V<sub>1</sub>—V<sub>2</sub>-(483)

B.P. 195-200° at 15 mm.

M.P. 46°

See 3:0585. Division A: Solids.

## — 3,5-DICHLOROBIPHENYL

 $C_{12}H_8Cl_2$ 

Beil. V —

V<sub>1</sub>—V<sub>2</sub>-(484)

B.P. 180° at 15 mm.

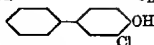
M.P. 36°

See 3:0360. Division A: Solids.

## — 2-CHLORO-4-PHENYLPHENOL

 $C_{12}H_9OCl$ 

Beil. S.N. 539



B.P. 176.6° at 5 mm.

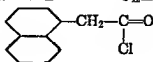
M.P. 77°

See 3:1900. Division A: Solids.

3:9856  $\alpha$ -NAPHTHYLACETYL CHLORIDE $C_{12}H_9OCl$ 

Beil. IX —

IX- (278)



B.P. 188° at 23 mm. (1)

180° at 17 mm. (7)

174° at 15 mm. (2)

148-155° at 0.5 mm. (3)

[For prepn. of  $\bar{C}$  from  $\alpha$ -naphthylacetic acid (1:0728) with  $PCl_5$  (4) (1), or with  $SOCl_2$  alone (2) (5) or in  $C_6H_6$  (6), see indic. refs.]

$\bar{C}$  with  $AlCl_3$  in nitrobenzene (1) (but not by  $SnCl_4$  in  $CS_2$  at room temp. (2)) losses  $HCl$  and ring-closes yielding acenaphthenone (1:5200), m.p. 121° cor. .

[ $\bar{C}$  with aminoacetic acid (glycine) yields (5) *N*-( $\alpha$ -naphthylacetyl) glycine, m.p. 153-154° (5). (For reactn. of  $\bar{C}$  with other amino acids and use as plant hormone see (5)).]

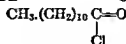
$\bar{C}$  on hydrolysis yields  $\alpha$ -naphthylacetic acid (1:0728) q.v. for the corresp. amide and anilide.

3:9856 (1) Badische Anilin- und Soda-Fabrik, Ger. 230,237, Jan. 20, 1910; *Cent.* 1911, I 358. (2) Cook, Hawett, *J. Chem. Soc.* 1933, 1106. (3) Wolfram, Schörnig, Hausdörfer (to I.G.), Ger. 562,391, Nov. 1, 1932; *Cent.* 1933, I 849. (4) Boessneck, *Ber.* 16, 641 (1883). (5) Isler (to Hoffmann-LaRoche Inc.), U.S. 2,179,979, Nov. 14, 1939; *C.A.* 34, 1808 (1940); *Brit.* 510,138, July 27, 1939; *Cent.* 1939, II 3572; *C.A.* 34, 4080 (1940); *Swiss* 203,078, May 16, 1939; *Cent.* 1939, II 8872. (6) Gilman, Kirby, *J. Am. Chem. Soc.* 51, 3477, Note 18 (1929). (7) King, Henshall, *J. Chem. Soc.* 1945, 418.

3:9858 *n*-DODECANOYL CHLORIDE $C_{12}H_{25}OCl$ 

Beil. II - 363

(n-Lauroyl chloride)



II- (159)

II- (321)

B.P. 175-176° at 47 mm. (1) M.P. - 17° (6)

150° at 22 mm. (2)

145-147° at 20 mm. (3)

145° at 18 mm. (4)

146-150° at 17 mm. (20)

143-148° at 16 mm. (5)

142.5° at 15 mm. (6)

140° at 15 mm. (7)

141° at 14 mm. (8)

134-137° at 11 mm. (9)

135-140° at 10 mm. (10)

134-137° at 11 mm. (11)

132° at 9 mm. (12)

 $n_D^{20} = 1.4458$  (7)

$\bar{C}$  is widely used as anti-moth agent and vapor fumigant but lit. and patents are so numerous that they cannot be included here; note, however, prevention of caking of  $\bar{C}$  by mixt. with 1-10% paraformaldehyde (43). — [For study of toxicity of  $\bar{C}$  see (44). — For use of  $\bar{C}$  in prepn. of sulfur dyes see (45).]

[For detn. of  $\bar{C}$  in air see (46); for detn. of  $\bar{C}$  in soil by means of detn. of refractive index of solns. in kerosene see (47).]

[For prepn. of  $\bar{C}$  from *p*-chloroaniline [Beil. XII-607, XII<sub>1</sub>-(304)] via diazotization, prepn. of diazonium/ $ZnCl_2$  double salt, and decompn. of latter in molten phenol (41% yield  $\bar{C}$  together with 31% hydroxybiphenyl + 15% diphenyl ether) see (48); from *p*-phenylenediamine [Beil. XIII-61, XIII<sub>1</sub>-(18)] via tetrazotization in AcOH (49) or  $H_3PO_4$  (50) with nitrosylsulfuric acid followed by subsequent reactn. with  $Cu_2Cl_2$  (yield: 70% (49) (50)) cf. (51), or by reduction with  $SnCl_2/HCl$  to *p*-phenylenedihydrazine and oxidn. with  $CuSO_4$  (52), see indic. refs.]

[For prepn. of  $\bar{C}$  from *p*-chloro-nitrobenzene [Beil. V-243, V<sub>1</sub>-(130)] with conc. HCl in s.t. at 270° (53), or with  $SOCl_2$  in s.t. at 160-200° (54) (55), see indic. refs.; from *p*-bromonitrobenzene [Beil. V-243, V<sub>1</sub>-(132)] (56), phenol-*p*-sulfonic acid [Beil. XI-241, XI<sub>1</sub>-(55)] (57), or *p*-chlorophenol (3:0475) (16) with  $PCl_5$  on hgt. see indic. refs.; from *p*-chlorobenzenesulfonic acid [Beil. XI-54, XI<sub>1</sub>-(14)] with  $SOCl_2$  in s.t. at 160-200° see (54) (55); from 2,5-dichlorobenzophenone (3:2340) by fusion with KOH/NaOH (65% yield) see (58); from di-*p*-chlorophenyl sulfide or di-*p*-chlorophenyl sulfoxide with S at 260-270° for 3-8 hrs. see (59); from *p*-chlorophenyl selenium trichloride by hgt. at 164° (90% yield) see (12).]

[For formn. of  $\bar{C}$  (together with *o*- and *m*-isomers in some cases) from  $C_6H_6$  with  $Cl_2$  in pres. of  $I_2$  (16),  $MoCl_5$  (60),  $AlCl_3$  (61), or conc.  $H_2SO_4$  (62), by electrolysis of susp. in AcOH + aq. HCl (69) or with aqua regia (70), see indic. refs.; from chlorobenzene (3:7903) with  $Cl_2$  + cat. at 600° (17) cf. (63), or with  $Cl_2$  in pres. of  $AlCl_3$  (65% yield (27)),  $FeCl_3$  (55% yield (27)), or Al/Hg (66), see indic. refs.; from chlorobenzene (3:7903) with  $Al_2S_2Cl_3$  (i.e.,  $2AlCl_3 + S_2Cl_2$  (64)) +  $SO_2Cl_2$  (64) (65), or by boulg. with  $FeCl_3$  (67), or in small amt. by hgt. with  $PbCl_4 \cdot 2NH_4Cl$  in s.t. at 210° (68), see indic. refs.]

[ $\bar{C}$  with  $Cl_2$  (61) in pres. of Al/Hg (66) or  $\bar{C}$  with  $Al_2S_2Cl_3$  (i.e.,  $2AlCl_3 + S_2Cl_2$ ) +  $SO_2Cl_2$  (64) gives (58% yield (64)) 1,2,4-trichlorobenzene (3:6420);  $\bar{C}$ , however, chlorinates less readily than *o*-dichlorobenzene (3:6035), and if their mixture or eutectic is chlorinated residual  $\bar{C}$  can be separated by fractional freezing (71) (72) (73). —  $\bar{C}$  with  $Cl_2$  in pres. of Fe (74) or with  $Al_2S_2Cl_3$  (i.e.,  $2AlCl_3 + S_2Cl_2$ ) +  $SO_2Cl_2$  as directed (64) gives (yields: 67% (64), 39% (74)) (75) 1,2,4,5-tetrachlorobenzene (3:4115). —  $\bar{C}$  with liq.  $Cl_2$  + sunlight + cat. (76) (77) or  $\bar{C}$  in  $CCl_4$  under 1% aq. NaOH in sunlight (76) adds  $3Cl_2$  yielding a mixt. of  $\beta$ - (m.p. 262° (76)) and  $\alpha$ - (m.p. 89.6° (76)) *p*-dichlorobenzene hexachlorides (use as insecticide (77)). — For study of photochem. chlorination of  $\bar{C}$  see (78).]

[ $\bar{C}$  when pure can be recovered unchanged after boiling with liq.  $Br_2$  (79); however,  $\bar{C}$  warmed with  $Br_2$  in pres. of Fe (79) or htd. with  $Br_2 + NaNO_2$  + fung.  $H_2SO_4$  in s.t. at 200° for 4 hrs. (80) gives (19% yield (79)) 2,5-dibromo-1,4-dichlorobenzene, ndls. from hot alc., m.p. 148° (79), 146° (80). —  $\bar{C}$  with excess  $Br_2 + AlCl_3$  as directed (81) gives 2,3,5,6-tetrabromo-1,4-dichlorobenzene, m.p. 278-278.5° (81) ]

[ $\bar{C}$  passed over Pt spiral at bright red heat yields (82) 2,5,2',5'-tetrachlorobiphenyl, m.p. 84-85° (82). —  $\bar{C}$  in EtOH at 55° in pres. of Adams' cat. ( $PtO_2$ ) with excess  $H_2$  at 3 atm. press. yields (83) cyclohexane (1:8405). —  $\bar{C}$  in alc. KCN with  $NiCl_2$  htd. in s.t. 20 hrs. at 260-270° gives (12% yield (84)) terephthalic acid (1:0910).]

[ $\bar{C}$  with Na + *n*-butyl chloride (3:7160) in xylene at 150° gives small yield (85) *p*-di-*n*-butylbenzene, b.p. 224-225.5° at 759 mm. (85). —  $\bar{C}$  with Mg +  $I_2$  (0.23 equiv.) gives in 6 hrs. 58% yield (86) *p*-chlorophenyl  $MgCl$ .]

$\bar{O}$  has also been much employed in the prepn. of mixed glycerides, but this topic cannot be expanded in detail in this text.

With phenols.  $\bar{O}$  on hgt. with phenols splits out HCl yielding the corresp. esters. [E.g.,  $\bar{O}$  with phenol (1:1420) gives (6) phenyl laurate, m.p. 24.5° (6), h.p. 210° at 15 mm. (6), 159–161° at 1 mm. (35);  $\bar{O}$  with p-cresol (1:1410) gives (6) p-tolyl laurate, m.p. 28° (6), h.p. 219.5° at 15 mm. (6). —  $\bar{O}$  (2 moles) with pyrocatechol (1:1520) at 110° for 2 hrs. gives (36) pyrocatechol dilaurate, m.p. 35.5°;  $\bar{O}$  (2 moles) with resorcinol (1:1530) at 110° for 2 hrs. gives (36) resorcinol dilaurate, m.p. 43–44.6°;  $\bar{O}$  (2 moles) with hydroquinone (1:1590) at 110° for 2 hrs. gives (36) hydroquinone dilaurate, m.p. 85–86°.]

[ $\bar{O}$  with phenol (1:1420) +  $AlCl_3$  in sym.-tetrachloroethane (3:6760) as solvent, however, gives (37) (35) (38) a mixt. of the corresp. hydroxylauropenones; viz., 32.6% yield (37) o-hydroxyphenyl undecyl ketone, m.p. 44–45.5° (corresp. 2,4-dinitrophenylhydrazones, m.p. 92–93°) and 24.6% yield (37) p-hydroxyphenyl undecyl ketone, m.p. 71–72° (corresp. 2,4-dinitrophenylhydrazones, m.p. 150–161°); for study of influence upon o/p ratio of use of nitrobenzene and  $CS_2$  as solvents see (38); for prepn. of these hydroxylauropenones from phenyl laurate by  $BF_3$  rearr. see (39); for their methyl ethers see (44).]

With salts of organic acids. [ $\bar{O}$  with Na laurate at 100° with protection from moist air gives (40) lauric anhydride (1:0601), m.p. 44° (41), 42.1° (42), 41.8° (43), 41° (40), but the latter is usually prepd. from lauric acid (1:0605) by hgt. with  $Ac_2O$  (41) (42) (43).]

With Grignard reagents.  $\bar{O}$  with  $RMgX$  reagents derived from tertiary halides not only undergoes the normal reaction to give the corresp. secondary alcohol but also suffers reduction [e.g.,  $\bar{O}$  with *ter*-BuMgCl gives (7) the expected 2,2-dimethyltetradecanol-3 (67% yield) together with lauryl alc. (1:5900) (13.7%) and *ter*-hutyl-undecyl-carbinyl laurate (10.4%); similarly,  $\bar{O}$  with *ter*-AmMgCl gives (7) lauryl alc. (1:5900) (54.8%) and 3,3-dimethylpentadecanol-4 (17.7%)].

With organic amines.  $\bar{O}$  with organic prim. amines gives (8) (9) (10) (11) (12) (13) (14) (15) (16) (17) (18) (19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30) (31) (32) (33) (34) (35) (36) (37) (38) (39) (40) (41) (42) (43) (44) (45) (46) (47) (48) (49) (50) (51) (52) (53) (54) (55) (56) (57) (58) (59) (60) (61) (62) (63) (64) (65) (66) (67) (68) (69) (70) (71) (72) (73) (74) (75) (76) (77) (78) (79) (80) (81) (82) (83) (84) (85) (86) (87) (88) (89) (90) (91) (92) (93) (94) (95) (96) (97) (98) (99) (100) (101) (102) (103) (104) (105) (106) (107) (108) (109) (110) (111) (112) (113) (114) (115) (116) (117) (118) (119) (120) (121) (122) (123) (124) (125) (126) (127) (128) (129) (130) (131) (132) (133) (134) (135) (136) (137) (138) (139) (140) (141) (142) (143) (144) (145) (146) (147) (148) (149) (150) (151) (152) (153) (154) (155) (156) (157) (158) (159) (160) (161) (162) (163) (164) (165) (166) (167) (168) (169) (170) (171) (172) (173) (174) (175) (176) (177) (178) 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Note that care must be taken to avoid confusion of  $\bar{C}$  with *n*-lauryl chloride (1-chlorododecane) (3:8810).

### PREPARATION OF $\bar{C}$

[For prepn. of  $\bar{C}$  from *n*-lauric acid (1:0605) with  $\text{PCl}_5$  (yields: 91.5% (10), 66% (13)) (6) (15) (32), with  $\text{PCl}_5 + \text{ZnCl}_2$  (45% yield (13)), with  $\text{PCl}_3$  (yields: 80% (8), 72% (13)) (4) (16), with  $\text{PCl}_3 + \text{ZnCl}_2$  (79% yield (13)), with  $\text{SOCl}_2$  (yields: 92% (9), 80–84% (11), 83% (13), 80% (20)) (1) (5) (17) (32) (33), with oxalyl (di)chloride (3:5060) (99% yield (3)) (2), or with carbonyl chloride (phosgene) (3:5000) at 140–150° (85–90% yield (18)) see indic. refs.]

[For prepn. of  $\bar{C}$  from  $\alpha,\beta$ -dichloroethyl laurate (19) on distn. with 0.1%  $\text{ZnCl}_2$  (chloroacetaldehyde (3:7212) is also formed) see (19).]

### CHEMICAL BEHAVIOR OF $\bar{C}$

#### BEHAVIOR WITH INORGANIC REACTANTS

Hydrogenation of  $\bar{C}$ . [ $\bar{C}$  with  $\text{H}_2 + \text{Pt}$  cat. at 200–320° and 50–180 mm. or with  $\text{H}_2 + \text{Raney Ni}$  at 160° and 50 mm. *fails* (8) to give the expected lauraldehyde (1:0017); this result is apparently due to side reactions of the latter since undecane (1:8820) and tricosane,  $\text{C}_{23}\text{H}_{48}$ , were isolated (8).]

Behavior with sodium. [ $\bar{C}$  (1 mole) with metallic sodium (1.2 moles) in dry ether refluxed (with stirring) for 4 hrs. gives (60% yield (20)) tetracosen-12-diol-12,13 dilaurate, i.e., the dilaurate ester of  $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{OH})=\text{C}(\text{OH})(\text{CH}_2)_{10}\text{CH}_3$ , *cryst.* from acetone/ $\text{C}_6\text{H}_6$  (3:1), m.p. 42–43° (20)]

Behavior with  $\text{Na}_2\text{O}_2$ . [ $\bar{C}$  with aq.  $\text{Na}_2\text{O}_2$  below 50° gives (21) dilauroyl peroxide, but no constants for either this prod. or for lauroyl hydrogen peroxide can be found in the literature; for use of dilauroyl peroxide as cat. for drying oils see (22).]

Behavior with  $\text{NaN}_3$ . [ $\bar{C}$  with  $\text{NaN}_3$  in  $\text{C}_6\text{H}_6$  reacts to give lauroyl azide (not isolated (23)), which loses  $\text{N}_2$  and rearr. giving (81–86% yield (23)) undecyl isocyanate, b.p. 103° at 3 mm. (23).]

#### BEHAVIOR WITH ORGANIC REACTANTS

With hydrocarbons. [ $\bar{C}$  with  $\text{C}_6\text{H}_6 + \text{AlCl}_3$  gives (yields: 100% (14), 71% (11)) (24) (25) (26) (27) phenyl undecyl ketone (laurophenone) [Beil. VII-345, VII-(186)], m.p. 47° (24) (28), 46° (14) (25), 45° (26), 44–45° (11); b.p. 222–223° at 21 mm. (25), 201–202° at 9 mm. (26), 193–194° at 9 mm. (11), 174° at 3 mm. (29) (corresp. oxime, m.p. 64.5° (11); semicarbazone, m.p. 98° (11); 2,4-dinitrophenylhydrazone, m.p. 101–102° (11)). — For analogous reactions of  $\bar{C}$  in pres. of  $\text{AlCl}_3$  with biphenyl (1:7175), diphenyl ether (1:7125), diphenylene oxide (1:7205), carbazole, thiophene, and furan see (30); for use of these products as waxes, addition agents for lubricants, etc., see (30) (31).]

With alcohols.  $\bar{C}$  with alcohols gives in general the corresp. alkyl laurates [e.g.,  $\bar{C}$  with  $\text{MeOH}$  gives methyl laurate, m.p. +5°, b.p. 148° at 18 mm. (10);  $\bar{C}$  with  $\text{EtOH}$  gives ethyl laurate (1:4196), m.p. –1.7 b.p. 269°; etc. —  $\bar{C}$  with benzyl alc. (1:6480) gives (32) benzyl laurate;  $\bar{C}$  with menthol (1:5940) gives (33) menthyl laurate; etc.].

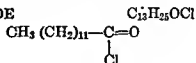
$\bar{C}$  (2 moles) with dihydric alcs. on htg. gives the corresp. neutral esters [e.g.,  $\bar{C}$  with ethylene glycol (1:6465) gives (34) ethylene glycol dilaurate (1:2157), m.p. 52°;  $\bar{C}$  with propanediol-1,2 (1:6455) gives (34) propylene glycol dilaurate, m.p. 35°;  $\bar{C}$  with butanediol-1,3 (1:6482) gives (34) 1,3-butylene glycol dilaurate, m.p. about 16.5°;  $\bar{C}$  with butanediol-1,4 (1:6516) gives (34) tetramethylene glycol dilaurate, m.p. 45.5°].

[For prepn. of  $\bar{C}$  from *m*-chlorobromobenzene [Beil. V-209, V<sub>1</sub>-(115), V<sub>2</sub>-(161)] (2) by conversion to *m*-chlorophenyl MgBr (cf. (3)) and reaction with *o*-chlorobenzonitrile [Beil. IX-336] (4) (5) followed by hydrolysis (73% yield) see (1).]

① 2,3'-Dichlorobenzophenone 2,4-dinitrophenylhydrazone: m.p. 255-257° (1).

3:9859-A (1) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1601-1602 (1945). (2) Hartwell, *Org. Syntheses* **24**, 23-24, Note 5 (1944). (3) Hein, Retter, *Ber.* **71**, 1968 (1938). (4) Norris, Klemka, *J. Am. Chem. Soc.* **62**, 1433 (1940). (5) Baudet, *Rec. trav. chim.* **43**, 707-708 (1924).

### 3:9860 TRIDECANOYL CHLORIDE



Beil. S.N. 162

B.P. 145-146° at 11 mm. (1)

145-147° at 10 mm. (2)

144-145° at 10 mm. (3)

[For prepn. of  $\bar{C}$  from tridecanoic acid (1:0600) with  $\text{SOCl}_2$  (3) (96.5% yield (2)) see indic. refs.]

[For reactn. of  $\bar{C}$  with  $\text{C}_6\text{H}_6 + \text{AlCl}_3$  yielding phenyl *n*-dodecyl ketone, m.p. 41-42°, b.p. 170° at 0.1 mm. (semicarbazone, m.p. 101°), see (3); for reactn. of  $\bar{C}$  with vanillylamine see (1); for reactn. of  $\bar{C}$  with 1,7-aminonaphthol see (4).]

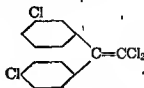
$\bar{C}$  on hydrolysis yields tridecanoic acid (1:0600) (for the amide, anilide, *p*-toluidide, and other derivatives corresp. to  $\bar{C}$  see 1:0600).

3:9860 (1) Ford-Moore, Phillips, *Rec. trav. chim.* **53**, 856-857 (1934). (2) Fierz-David, Kuster, *Helv. Chim. Acta* **22**, 86-89, 101 (1939). (3) Ziegler, Dersch, Wollthan, *Ann.* **511**, 38-39 (1934).

### 3:9863 1,1-DICHLORO-2-(*m*-CHLOROPHENYL)-2-(*p*-CHLOROPHENYL)ETHYLENE

$\text{C}_{14}\text{H}_8\text{Cl}_4$

Beil. S.N. 480



B.P. 158-162° at 1 mm. (1)

[For prepn. of  $\bar{C}$  from "*m,p*-DDT" (3:9867) by elimination of 1 HCl with alc. KOH (80% yield) see (1).]

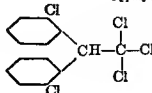
$\bar{C}$  on oxidn. with  $\text{CrO}_3$  gives (41% yield (1)) 3,4'-dichlorobenzophenone (3:3415), m.p. 113°.

3:9863 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1600 (1945).

### 3:9865 1,1,1-TRICHLORO-2,2-bis-(*o*-CHLOROPHENYL)ETHANE ("o,o'-DDT")

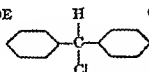
$\text{C}_{14}\text{H}_9\text{Cl}_5$

Beil. S.N. 479



... Staudinger (to Armour and Co.), U.S. 2,033,544, March 10, 1936; *Cent* 1936, 107, 363 (1921). {33} Staudinger, Schwalenstöcker, *Ber.* 68, 725-742 (1937/5); *Cent.* 1939, 1 95-96; *C.A.* 34, 6934 (1940). {37} Ralston, Bauer, *J. Org. Chem.* 5, 165-170 (1940). {38} Ralston, Ingle, McCorkle, *J. Org. Chem.* 7, 457-461 (1942). {39} Balle, Heimke (to I.G.), *Ger.* 637,808, Nov. 4, 1936; *Chem. Abstr.* 31, 2222 (1937).

## — BENZOHYDRYL CHLORIDE

 $C_{13}H_{11}Cl$ 

Beil. V - 590

 $V_1-(278)$  $V_2-(500)$ 

B.P. 190-191° at 247 mm.

M.P. 18°

 $D_4^{19.5} = 1.1308$  $n_D^{19.5} = 1.5959$ 

See 3:0060. Division A: Solids.

3:9859 1-CHLOROTRIDECAENE  
(*n*-Tridecyl chloride) $CH_3(CH_2)_{11}CH_2Cl$  $C_{13}H_{27}Cl$ 

Beil. S.N. 10

B.P. 135.7-136.0° at 9 mm. (1)

 $D_4^{20} = 0.8668$  (1)  $n_D^{20} = 1.4460$  (1)

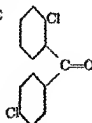
[For prepn. of  $\bar{C}$  from *N*-benzoyl-*n*-tridecylamine (*N*-(*n*-tridecyl)benzamide) with  $PCl_5$  at 160-210° (67% yield) see (1).]

$\bar{C}$  with Mg in dry ether gives *n*- $C_{13}H_{27}MgCl$  (1) [this prod. with allyl bromide as directed gives (43% yield (1)) hexadecene-1 (cetene) (1.7000)].

— *n*-Tridecyl *p*-nitrobenzoate: m.p. 37.4° cor. (2). [Prepd indirectly (2).]— *n*-Tridecyl 3,5-dinitrobenzoate: unreported— *N*-(*n*-Tridecyl)phthalimide: unreported

3:9859 (1) Suida, Drahowzal, *Ber.* 75, 996 (1942) (2) Armstrong, Copenhagen, *J. Am. Chem. Soc.* 65, 2252-2253 (1943).

## — 2,4'-DICHLOROBENZOPHENONE

 $C_{13}H_8OCl_2$ 

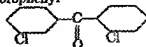
Beil. VII - 420

VII<sub>1</sub>—

B.P. 214-215° at 22 mm.

M.P. 66-67°

See 3:1565. Division A: Solids.

3:9859-A 2,3'-DICHLOROBENZOPHENONE  
(*o*-Chlorophenyl *m*-chlorophenyl  
ketone) $C_{13}H_8OCl_2$ 

Beil. S.N. 652

B.P. 140-142° at 1 mm. (1)



Oil, which on attempted distillation dec. (1) (2) into HCl + 1,2-diphenylethylene (stilbene) (1:7250). —  $\bar{C}$  can, however, be distilled with steam (1).

[For prepn. of  $\bar{C}$  from  $C_6H_6$  with chloroacetaldehyde (3:7212) (generated in mixt. by use of  $\alpha,\beta$ -dichloroethyl ethyl ether (3:5640)) + conc.  $H_2SO_4$  see (2); for formn. in very small amt. from 1,1,1-trichloro-2,2-diphenylethane [Beil. VI-606, VI-(285)] during electrolytic reduction in alc./HCl see (3).]

$\bar{C}$  with alc. KOH loses HCl yielding (1) 1,1-diphenylethylene [Beil. V-639, V-(308), V<sub>2</sub>-(543)], b.p. 277°, accompanied by its polymers.

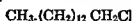
3:9871 (1) Hepp, *Ber.* 7, 1409-1413 (1874). (2) Hepp, *Ber.* 6, 1439 (1873). (3) Brand, *Z. Elektrochem.* 16, 670 (1910).

### 3:9874 1-CHLOROTETRADECANE



Beil. I —

(*n*-Tetradecyl chloride;



I<sub>1</sub>—

*n*-myristyl chloride)

I<sub>2</sub>-(135)

B.P. 154-155° at 15 mm. (1)

$D_4^{20} = 0.8589$  (2)  $n_D^{20} = 1.4450$  (2)

139-142° at 4 mm. (2)

44-53° at  $2 \times 10^{-4}$  mm. (2)

Care must be taken to avoid confusion of  $\bar{C}$  with the acid chloride of *n*-tetradecanoic acid (myristic acid), commonly designated as *n*-myristoyl chloride (3:9885).

[For prepn. of  $\bar{C}$  from tetradecanol-1 (1:5935) with conc. HCl +  $ZnCl_2$  or by btg. in s.t. with fuming HCl see (1); for formn. of  $\bar{C}$  (31% yield) from tetradecanol-1 (1:5935) with  $PCl_3$  in pres. of mesityl oxide and  $Ac_2O$  see (2).]

[ $\bar{C}$  (1 mole) with pyridine (1 mole) in s.t. at 110° for 15 hrs. gives (3) the corresp. quaternary salt, viz., *N*-(*n*-tetradecyl)pyridinium chloride, cryst. from alc./ether or from  $C_6H_6$  as monohydrate, m.p. 85.5° (3), 75.5° (5) (this prod. on cat. hydrogenation gives (3) *N*-(*n*-tetradecyl)piperidinium hydrochloride, m.p. 186-187° (3). — For analogous reactn. of  $\bar{C}$  with isoquinoline see (3) ]

[For study of rate of reactn. of  $\bar{C}$  with KI in acetone at 50° and 60° see (1).]

— *n*-Tetradecyl *p*-nitrobenzoate: m.p. 51.2° cor. (4). [Prepd. indirectly.]

— *n*-Tetradecyl 3,5-dinitrobenzoate: unreported.

— *N*-(*n*-Tetradecyl)phthalimide: unreported.

— *S*-(*n*-Tetradecyl)isothioureia picrate: unreported.

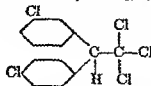
— *n*-Tetradecyl mercuric chloride: unreported (but see (6)).

3:9874 (1) Conant, Hussey, *J. Am. Chem. Soc.* 47, 483, 485 (1925). (2) Drake, Marvel, *J. Org. Chem.* 2, 394 (1937). (3) Karrer, Kahnt, Epstein, Jaffé, Ishii, *Helv. Chim. Acta* 21, 233-234 (1938). (4) Armstrong, Copenhaver, *J. Am. Chem. Soc.* 65, 2252-2253 (1943). (5) Lottermoser, Froscher, *Kolloid-Beihfte* 45, 305-306, 316, 319, 323, 339 (1937). (6) Meals, *J. Org. Chem.* 9, 215 (1944).

This compound is the so-called  $\alpha,\alpha'$ -isomer of "DDT" (3:3298). Although it is known to be a contaminant of "DDT" (e.g., 6% (1)) no accurate information regarding it is at present available.

3:9865 (1) Gunther, *J. Chem. Education* 22, 239 (1945).

3:9867 1,1,1-TRICHLORO-2-(*m*-CHLOROPHENYL)-2-(*p*-CHLOROPHENYL)ETHANE  $C_{14}H_7Cl_5$  Beil. S.N. 479  
(" *m,p'*-DDT ")



B.P. 181-185° at 1 mm. (1)

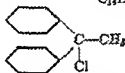
[For prepn. of  $\bar{C}$  from 2,2,2-trichloro-1-(*m*-chlorophenyl)ethanol (1) by condensation with chlorobenzene (3:7903) in presence of fuming  $H_2SO_4$  (48% yield) see (1).]

[ $\bar{C}$  with alc. KOH loses HCl giving (80% yield (1)) 1,1-dichloro-2-(*m*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene (3:9863).]

$\bar{C}$  on dinitration with equal wt. fuming  $HNO_3$  gives (90% yield (1)) a dinitro cpd., m.p. 118.8-120.1° (1).

3:9867 (1) Haller, Bartlett, Drake, Newman, Cristol, *J. Am. Chem. Soc.* 67, 1600 (1945).

3:9870 1,1-DIPHENYLETHYL CHLORIDE  $C_{14}H_{13}Cl$  Beil. S.N. 479  
(Chloro-diphenyl-methyl-methane)



[See also 2,2-diphenylethyl chloride (3:9871).]

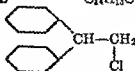
$\bar{C}$  cannot be obtd. in cryst. form; at room temp.  $\bar{C}$  slowly dec. (1) to give HCl and 1,1-diphenylethylene [Beil. V-639, V<sub>1</sub>-(308), V<sub>2</sub>-(543)], b.p. 277°, accompanied (1) (3) by a small amt. of 1,1,3,3-tetraphenylbutene-1, m.p. 113-114° (the unsatd. dimer of 1,1-diphenylethylene).

[For prepn. of  $\bar{C}$  from diphenyl-methyl-carbinol [Beil. VI-685, VI<sub>1</sub>-(330)] in  $C_6H_6$  (1) or pet. ether (2) in pres. of  $CaCl_2$  by saturation at 0-10° with dry HCl gas and stdg. overnight see indic. refs.]

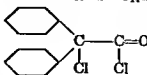
$\bar{C}$  in  $C_6H_6$  stood at room temp. gives (95-97% yield in 1 week, 80% in 1 day (1)) 1,1,3-triphenyl-3-methylhydri-dene (the saturated dimer of 1,1-diphenylethylene), colorless cryst. from alc., m.p. 143° (1); note that attempts to accelerate this reaction by warming give decreased yield together with formation of 1,1-diphenylethylene and its unsaturated dimer (mentioned above).

3:9870 (1) Schoepfle, Ryan, *J. Am. Chem. Soc.* 52, 4025-4027 (1930). (2) Schoepfle, Ryan, *J. Am. Chem. Soc.* 54, 3692 (1932). (3) Blicke, Powers, *J. Am. Chem. Soc.* 52, 3383 (1930).

3:9871 2,2-DIPHENYLETHYL CHLORIDE  $C_{14}H_{13}Cl$  Beil. V - 606  
V<sub>1</sub>-(285)  
V<sub>2</sub>-



[See also 1,1-diphenylethyl chloride (3:9870).]

—  $\alpha$ -CHLORO-DIPHENYLACETYL CHLORIDE  $C_{14}H_{10}OCl_2$ Beil. IX - 675  
IX<sub>1</sub>-(283)

B.P. 180° at 14 mm. M.P. 50°

See 3:0885. Division A: Solids.

3:9885 *n*-TETRADECANOYL CHLORIDE  $C_{14}H_{27}OCl$   
(*n*-Myristoyl chloride)  $CH_3(CH_2)_{12}C(=O)Cl$ Beil. II - 368  
II<sub>1</sub>-(162)  
II<sub>2</sub>-(329)

B.P. 195°	at 45-47 mm. (1)	M.P. -1° (7)
179-180°	at 22 mm. (2)	
175-176°	at 16-17 mm. (3)	
174°	at 16 mm. (4)	
169°	at 15 mm. (5)	
168°	at 15 mm. (6) (7)	
160-162°	at 11 mm. (8)	
159-161°	at 11 mm. (9)	
134°	at 2.5 mm. (10)	
119.5-123°	at 1 mm. (11)	

Care must be taken to avoid confusion of  $\bar{C}$  with *n*-myristyl chloride (1-chlorotetradecane) (3:9874).PREPARATION OF  $\bar{C}$ 

[For prepn. of  $\bar{C}$  from myristic acid (1:0630) with  $SOCl_2$  (yields: 91% (8), 80% (3), 80-84% (9), 79% (6)) (12) (2) (13) (14) (15); with  $PCl_5$  (89% yield (6)) (7) (14); with  $PCl_3$  (11) (1) (17); with  $PCl_3 + ZnCl_2$  (79% yield (6)); or with oxalyl (di)chloride (3:5060) (10) see indic. refs.]

CHEMICAL BEHAVIOR OF  $\bar{C}$ 

## BEHAVIOR WITH INORGANIC REACTANTS

Hydrogenation of  $\bar{C}$ . [ $\bar{C}$  with  $H_2 + Pt$  cat. at 220-230° at 60-65 mm. gives (1) not only some *n*-myristaldehyde (1:0004) and its trimer but also (by loss of CO from  $\bar{C}$ ) *n*-tridecane [Beil. 1-171, I<sub>2</sub>-(134)], b.p. 234°.]

Hydrolysis of  $\bar{C}$ .  $\bar{C}$  on hydrolysis with aq. presumably yields myristic acid (1:0630) + HCl although actual record of this reaction is lacking in the literature.

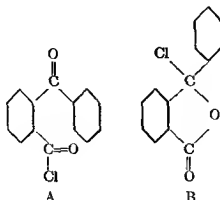
Behavior with sodium. [ $\bar{C}$  (1 mole) with metallic sodium (1.2 moles) in dry ether refluxed (with stirring) for 10 hrs. gives (64% yield (3)) octacosen-14-diol-14,15 dimyristate, i.e., the dimyristate ester of  $CH_3(CH_2)_{12}C(OH)=C(OH)(CH_2)_{12}CH_3$ , cryst. from acetone/ $C_6H_6$  (3:1), m.p. 54-55° (3).]

## BEHAVIOR WITH ORGANIC REACTANTS

With hydrocarbons (or their equivalents). [ $\bar{C}$  with  $C_6H_6 + AlCl_3$  in  $CS_2$  gives (69% yield (9)) phenyl *n*-tridecyl ketone (myristophenone) [Beil. VII<sub>1</sub>-(186)], m.p. 52-53°

3:9880 *o*-BENZOYL-BENZOYL CHLORIDE=A  
 3-CHLORO-3-PHENYLPHTHALIDE=B  
 (*o*-Benzoylbenzoyl *pseudo*-chloride)

$C_{14}H_9O_2Cl$  A. Beil. X-749  
 $X_1$ —  
 B. Beil. XVII-361  
 $XVII_1$ —



$\bar{C}$  appears to react in two tautomeric forms correspond to structures A and B, the independent existence of which, however, has not (as yet) been definitely established. The same method of prepn. has in various laboratories given results sometimes suggesting a preponderance of A, sometimes of the tautomer B. The constants reported for  $\bar{C}$  show a correspondingly wide variation, e.g., m p. 82–83° (1), aht. 70° (2), 59–60° (3), b p. 170–171° at 1 mm. (1); other workers, e.g. (5) (6), have sometimes obtd.  $\bar{C}$  in crystn form and sometimes not and have failed to report constants

[For prepn. of  $\bar{C}$  from *o*-benzoylbenzoic acid (1·0720) with  $PCl_5$  in  $CS_2$  (2) (3) (4) (5), or  $PCl_5$  (7),  $PCl_5$  (7) (4), or  $SOCl_2$  (7) (4) (5) (6) (1) (8) (11), see indic. refs.; for prepn. of  $\bar{C}$  from 3-phenylphthalide with  $Cl_2$  at 115–120° see (5) ]

$\bar{C}$ -A on htg. above 130° loses HCl and ring-closes yielding (9) (10) anthraquinone (1:0095).

$\bar{C}$ -A with conc. aq.  $NH_4OH$  at 0° yields (9) *o*-benzoylbenzamide, m p 165° cor. (9), with aniline yields (11) *o*-benzoylbenzanilide, m p 195° (11).

$\bar{C}$ -A with MeOH yields (2) (7) (4) methyl *o*-benzoylbenzoate, m p 51·5° (4), 51·7° (4), 51–52° (2), 52° (12);  $\bar{C}$ -B with MeOH yields (7) methyl *pseudo*-*o*-benzoylbenzoate (3-methoxy-3-phenylphthalide), m p 80–81° (7)

$\bar{C}$ -A with EtOH should yield ethyl *o*-benzoylbenzoate, m p. 58° (13) (12);  $\bar{C}$ -B with EtOH yields (14) ethyl *pseudo*-*o*-benzoylbenzoate (3-ethoxy-3-phenylphthalide), m p. 51–53° (14), 56° (13).

$\bar{C}$ -A with K phenolate or with phenol in pyridine yields (5) phenyl *o*-benzoylbenzoate, m p. 162–163° (5),  $\bar{C}$ -B under same circumstances yields phenyl *pseudo*-*o*-benzoylbenzoate (3-phenoxy-3-phenylphthalide), m.p. 80–82° (5). [For analogous behavior of other phenols see (5).]

$\bar{C}$ -B with phenol yields (6) 3-(*p*-hydroxyphenyl)-3-phenylphthalide, m p. 168–170° (6). [For analogous reactn. with other phenols and phenol ethers see (6) ]

[For reactn. of  $\bar{C}$  with  $\alpha$ -methylnaphthalene see (15).]

3:9880 (1) Norris, Ware, *J. Am. Chem. Soc.* **61**, 1418–1420 (1938) (2) Haller, Guyot, *Bull. soc. chim.* (3) **25**, 49–56 (1901) (3) Martin, *J. Am. Chem. Soc.* **38**, 1142–1144 (1916) (4) McMullen, *J. Am. Chem. Soc.* **38**, 1228–1230 (1916) (5) Blicke, Swisher, *J. Am. Chem. Soc.* **56**, 902–904 (1934). (6) Blicke, Swisher, *J. Am. Chem. Soc.* **56**, 923–925 (1934). (7) Meyer, *Monatsh.* **25**, 475–486 (1904). (8) Sandahl, Christiansen, *Bull. soc. chim.* (5) **5**, 1577 (1938). (9) Gräbe, Ullmann, *Ann.* **291**, 10–12 (1896). (10) Meyer, *Monatsh.* **25**, 1181–1184 (1904).

(11) Meyer, *Monatsh.* **28**, 1226–1227 (1907). (12) Plascuda, *Ber.* **7**, 987 (1874). (13) von Auwers, Henze, *Ber.* **52**, 599 (1919). (14) Egerer, Meyer, *Monatsh.* **34**, 77–79 (1913). (15) Clar, *Ber.* **63**, 116 (1930)

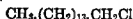
{11} Ralston, Bauer, *J. Org. Chem.* **5**, 168-169 (1940). {12} Marangoni, *Atti ist. Veneto sci.*, 95-96; *C.A.* **34**, 6934 (1940). {13} Asano, *Cent.* **1931**, II 1867; *C.A.* **25**, 4267 (1931). {15} Brauns, *J. Am. Chem. Soc.* **42**, 1479 (1920). {16} Blau, *Monatsh.* **26**, 95-99 (1905). {18} Ralston, Christensen, *Ind. Eng. Chem.* **29**, 194-196 (1937). {19} Ralston, McCorkle, Bauer, *J. Org. Chem.* **5**, 653, 658 (1940). {20} Staudinger, Schwalenstöcker, *Ber.* **68**, 732-741 (1935). {21} Krafft, Rosiny, *Ber.* **33**, 3577-3578 (1900). {22} Wallace, Copenhaver, *J. Am. Chem. Soc.* **63**, 699 (1941). {23} Holde, Gentner, *Ber.* **58**, 1423 (1925).

## 3:9800 1-CHLOROPENTADECANE



Beil. I —

(n-Pentadecyl chloride)

I<sub>1</sub>-(68)I<sub>2</sub>-(136)

B.P. 168-171° at 10 mm. (1)

 $D_{25}^{25} = 0.8433$  (2)  $n_D^{25} = 1.4470$  (2)

[For prepn. of  $\bar{C}$  from *N*-benzoyl-*n*-pentadecylamine (*N*-(*n*-pentadecyl)benzamide) with  $PCl_5$  on distn. (58% yield) see (1); from *n*- $C_{12}H_{25}MgBr$  (1 mole) by reactn. in ether with  $\gamma$ -chloro-*n*-propyl *p*-toluenesulfonate (2 moles) (yield 42% on  $RMgBr$ ) (note that some 1-bromo-3-chloropropane, b.p. 138-140°, is also formed) see (2).]

[ $\bar{C}$  with excess aniline at 100° for a long time, then treated with dil. HCl, ppts. (1) *N*-(*n*-pentadecyl)aniline HCl, cryst. from alc./ether, m.p. 97° (1); free base, m.p. 36° (1).]

— *n*-Pentadecyl *p*-nitrobenzoate: m.p. 45.8° cor. (3). [Prepd. indirectly.]

— *n*-Pentadecyl 3,5-dinitrobenzoate: unreported.

— *N*-(*n*-Pentadecyl)phthalimide: unreported.

— *S*-(*n*-Pentadecyl isothiurea) picrate: unreported.

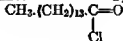
— *n*-Pentadecyl mercuric chloride: unreported.

3:9890 (1) von Braun, Solecki, *Ber.* **44**, 1472 (1911). (2) Rossander, Marvel, *J. Am. Chem. Soc.* **50**, 1495 (1928). (3) Armstrong, Copenhaver, *J. Am. Chem. Soc.* **65**, 2252-2253 (1943).

## 3:9000 PENTADECANOYL CHLORIDE



Beil. S.N. 162



B.P. 172-176° at 10 mm. (1)

157° at 5 mm. (2)

[For prepn. of  $\bar{C}$  from pentadecanoic acid (1:0620) with  $SOCl_2$  (97% yield (1)) see (1).

[For reactn. of  $\bar{C}$  with vanillylamine see (2); with 1,7-aminonaphthol see (1).]

$\bar{C}$  on hydrolysis yields pentadecanoic acid (1:0620) q v. (for the amide, anilide, and other derivatives corresp. to  $\bar{C}$  see 1:0620).

3:9900 (1) Fierz-David, Kuster, *Helv. Chim. Acta* **22**, 86-89, 101 (1939). (2) Ford-Moore, Phillips, *Rec. trav. chim.* **53**, 857 (1934).

## — 1-CHLOROHEXADECANE



Beil. I - 172

(n-Hexadecyl chloride;

cetyl chloride)

I<sub>1</sub>—I<sub>2</sub>-(138)

B.P. 289° dec.

M.P. 15°

See 3:0015. Division A: Solids.

(corresp. oxime, m.p. 60.5°; corresp. 2,4-dinitrophenylhydrazone, m.p. 98.0-98.5°; corresp. semicarbazone, m.p. 101° (9)).]

[ $\bar{C}$  with thiophene +  $\text{SnCl}_4$  gives (yield not stated (18)) 2-furyl *n*-tridecyl ketone (2-myristolythiophene), oil, b.p. 205-210° at 4 mm.,  $D_{25}^{25} = 0.9506$ ,  $n_D^{25} = 1.4961$  (18).]

[ $\bar{C}$  with carbazole +  $\text{AlCl}_3$  gives (yield not stated (18)) 2,8-dimyristolylcarbazole, m.p. 169° (18).]

With alcohols.  $\bar{C}$  with alcohols gives in general the corresp. alkyl myristates. [E.g.,  $\bar{C}$  with MeOH gives methyl myristate (1:2013), m.p. 18.5°;  $\bar{C}$  with EtOH gives ethyl myristate (1:4316), m.p. 11.9°, b.p. 295°; etc. —  $\bar{C}$  with benzyl alc. (1:6480) gives (14) benzyl myristate;  $\bar{C}$  with menthol (1:5940) gives (15) menthyl myristate; etc.]

$\bar{C}$  (2 moles) with dihydric alcs. on htg. gives the corresp. neutral esters [e.g.,  $\bar{C}$  with ethylene glycol (1:6465) gives (20) ethylene glycol dimyristate (1:2233), m.p. 63°;  $\bar{C}$  with propanediol-1,2 (1:6455) gives (20) propylene glycol dimyristate, m.p. 41.5°;  $\bar{C}$  with butanediol-1,3 (1:6482) gives (20) 1,3-butylene glycol dimyristate, m.p. 29.5-31.0°;  $\bar{C}$  with butanediol-1,4 (1:6516) gives (20) tetramethyleneglycol dimyristate, m.p. 55°].

$\bar{C}$  has been much employed in prepn. of mixed glycerides, but this topic cannot be expanded in detail in this text [however, for examples of use of  $\bar{C}$  with the compound of glycerol + acetone (i.e., 4-hydroxymethyl-2,2-dimethyldioxolane-1,3) in prepn. of glyceryl  $\alpha$ -monomyristate (" $\alpha$ -monomyristin") see (10) (5)].

With phenols.  $\bar{C}$  on htg. with phenols splits out  $\text{HCl}$  yielding the corresp. esters [e.g.,  $\bar{C}$  with phenol (1:1420) on htg. gives (7) phenyl myristate, m.p. 36°, b.p. 230° cor. at 15 mm. (7);  $\bar{C}$  with *p*-cresol (1:1410) on htg. gives (7) *p*-tolyl myristate, m.p. 39°, b.p. 239.5° at 15 mm. (7);  $\bar{C}$  (2 moles) with pyrocatechol (1:1520) at 110° for 2 hrs. gives (12) pyrocatechol dimyristate, m.p. 47-48°;  $\bar{C}$  (2 moles) with resorcinol (1:1530) at 110° for 2 hrs. gives (12) resorcinol dimyristate, m.p. 53°;  $\bar{C}$  (2 moles) with hydroquinone (1:1590) at 110° for 2 hrs. gives (12) hydroquinone dimyristate, m.p. 90-90.3°].

[ $\bar{C}$  with phenol (1:1420) +  $\text{AlCl}_3$  in *sym*-tetrachloroethane (3:5750) as solvent, however, gives (11) a mixt. of the corresp. hydroxymyristophenones: viz., 31.9% yield (11) *o*-hydroxyphenyl *n*-tridecyl ketone, m.p. 52-55° (corresp. 2,4-dinitrophenylhydrazone, m.p. 92.0-92.5°) and 36.7% yield (11) *p*-hydroxyphenyl *n*-tridecyl ketone, m.p. 78-80° (corresp. 2,4-dinitrophenylhydrazone, m.p. 142-143°); for prepn. of these same products by direct rearr. of phenyl myristate (above) with  $\text{AlCl}_3$  in *sym*-tetrachloroethane soln. see (19).]

With salts of organic acids. [ $\bar{C}$  with sodium myristate at 100° in absence of air gives (21) myristic anhydride (1:0629), m.p. 53.6° (22), 53.4° (23), 51° (21).]

With organometallic compounds. [ $\bar{C}$  with ethyl sodioacetoacetate gives (60% yield (13)) ethyl  $\alpha$ -myristoylacetoacetate, b.p. 170-183° at 3 mm.; this prod. with  $\text{NH}_3$  gas splits off the aceto group yielding (13) ethyl myristoylacetate, m.p. 36-37°, b.p. 187-188° at 7 mm.]

With organic amines.  $\bar{C}$  with organic primary amines yields the corresp. amides [e.g.,

$\bar{C}$  with *p*-cyimidine

anilide, m.p. 88-89

*N*-(vanillyl)myristamide,  $\alpha$ -form, m.p. 82°,  $\beta$ -form, m.p. 76.5-77°].

$\bar{C}$  on hydrolysis yields myristic acid (1:0630), m.p. 53.86°; for the amide, anilide, *p*-toluidide, and other derivatives corresp. to  $\bar{C}$  see myristic acid (1:0630).

3:9885 (1) Escourrou, *Bull. soc. chim.* (5) 6, 1177, 1180 (1939). (2) Hann, Jamieson, *J. Am. Chem. Soc.* 50, 1443 (1928). (3) Halston, Selby, *J. Am. Chem. Soc.* 61, 1010-1020 (1939). (4) Ford-Moore, Phillips, *Rec. trav. chim.* 53, 857 (1934). (5) Rewadikar, Watson, *J. Indian Inst. Sci.* A-13, 125-140 (1939). (6) 1930, 11 3737; C.A. 25, 613 (1931). (6) Clark, Bell, *Trans. Roy. Soc. Can.* (3) 27, 111 97-103 (1933). (7) Kraft, Bürger, *Ber.* 17, 1378-1380 (1894). (8) Lues-David, Kuster, *Helv. Chim. Acta* 22, 59 (1939). (9) Ju, Shen, Wood, *J. Inst. Petroleum Tech.* 26, 514-520 (1940). (10) Averill, Roche, King, *J. Am. Chem. Soc.* 51, 868 (1929).

[ $\bar{C}$  with ethylene +  $AlCl_3$  gives a mixt. (87) of mono-, di-, tri-, and tetra-ethyl-*p*-dichlorobenzenes.]

[ $\bar{C}$  (3 moles) with  $CHCl_3$  (1 mole) +  $AlCl_3$  gives (14% yield (88)) *tris*-(2,5-dichlorophenyl)methane, colorless cryst. from  $C_6H_6$ , m.p. 206–208° (88). —  $\bar{C}$  with  $CCl_4$  +  $AlCl_3$  at room temp. (88) or in  $CS_2$  (89) (90) gives (26% yield (88)) 2,5,2',5'-tetrachlorobenzophenone dichloride, m.p. 173–174° (89) (88); this with dil. alc. on boilg. or htg. in s.t. at 130° hydrolyzes to 2,5,2',6'-tetrachlorobenzophenone, colorless cryst. from alc., m.p. 128° (89) (90). —  $\bar{C}$  with  $CCl_4$  +  $AlCl_3$  at 55° for 10 hrs. presumably first yields *tris*-(2,5-dichlorophenyl)methyl chloride (not isolated) which then loses 1 HCl giving (23% yield (88)) 1,4,7-trichloro-9-(2,5-dichlorophenyl)fluorene (?), m.p. 179–180° (88).]

[ $\bar{C}$  with acetyl chloride (3:7065) +  $AlCl_3$  gives (91) 2,5-dichloroacetophenone, b.p. 251° at 756 mm., m.p. 14° (91) (oxime, m.p. 130°, via Beckmann rearr. with conc.  $H_2SO_4$  gives acet-2,5-dichloroanilide, m.p. 133° (91)). —  $\bar{C}$  with benzoyl chloride (3:6240) +  $AlCl_3$  yields (91) (92) 2,5-dichlorobenzophenone, white ndls. from alc., m.p. 88° (91), 85–86° (92) (oxime, m.p. on slow htg. 207°, via Beckmann rearr. with conc.  $H_2SO_4$  gives benz-2,5-dichloroanilide, m.p. 122° (91)). —  $\bar{C}$  with *o*-chlorobenzoyl chloride (3:6640) +  $AlCl_3$  gives (92) 2,2',5-trichlorobenzophenone, m.p. 145–147° (92). —  $\bar{C}$  with 2,4-dichlorobenzoyl chloride +  $AlCl_3$  gives 2,5,2',4'-tetrachlorobenzophenone, m.p. 176° (92).] — [Note that  $\bar{C}$  fails to react with *sym*-dichlorodimethyl ether (3:5245).]

[ $\bar{C}$  with phthalic anhydride (1:0725) +  $AlCl_3$  gives (59.3% (94), 27% (93))  $\delta$ -(2,5-dichlorobenzoyl)benzoic acid, colorless pr. from  $C_6H_6$ , m.p. 169° cor. (93), 167° (94); this prod. on ring closure with fuming  $H_2SO_4$  (94) or conc.  $H_2SO_4$  (93) at 150° gives (yields: 83.5% (94), 83% (93)) 1,4-dichloroanthraquinone [Beil. VII-787, VII-(411)], or-yel. ndls. from AcOH, m.p. 187.5° cor. (93), 186° (94). — Note that  $\bar{C}$  reacts with phthalic anhydride +  $AlCl_3$  less readily than *o*-dichlorobenzene (3:6055) (use in sepa. of the two isomers (95)). — For corresp. condens. of  $\bar{C}$  with 3-sulphophthalic anhydride and 4-sulphophthalic anhydride in pres. of  $AlCl_3$  see (96).]

[ $\bar{C}$  on partial hydrol. with aq. MeOH alk., alk. carbonates, or best alk. earths in pres. of Cu or Cu salts at elevated temps. under press. gives in excellent yield (98) (99) (100) (101) (102) (103) (104) (105) *p*-chlorophenol (3:0475) (some phenol (1:1420) is also formed (102)); if the hydrolysis of  $\bar{C}$  is carried further (100) (106) hydroquinone (1:1690) is also obtd.] — [For study of kinetics of reactn. of  $\bar{C}$  with MeOH/alk. see (99) (107) (108).]

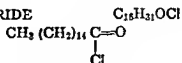
[ $\bar{C}$  with anhyd.  $NH_3$  in alc. in pres. of  $CuCl_2$  + Cu under press. at 150–200° yields (109) *p*-chloroaniline [Beil. XII-607, XII-(304)];  $\bar{C}$  with conc. aq.  $NH_4OH$  in pres. of CuO under press. at 150–200° gives (110) (111) (112) (113) (114) *p*-phenylenediamine [Beil. XIII-61, XIII-(18)]. — [ $\bar{C}$  with K diphenylamine at 240–245° gives (115) not only the expected *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine, tbls. from acetone, m.p. 199–200°, but also by rearr. *N,N,N',N'*-tetraphenyl-*m*-phenylenediamine, m.p. 137.5–138°.]

[ $\bar{C}$  on mononitration, e.g., with 5 wt. pts. abs.  $HNO_3$  at 0° (116) (99), with 2 wt. pts.  $HNO_3$  ( $D = 1.48$ ) below 50° (120), or with 1.5 pts. of a mixt. contg. 2 pts.  $HNO_3$  ( $D = 1.54$ ) + 3 pts. conc.  $H_2SO_4$  (117) (118) (119) at 70–100° for 30–60 min., yields 1,4-dichloro-2-nitrobenzene [Beil. V-245, V-(131)], cryst. from alc., m.p. 55° (120), 54.5° (99), 54° (119), 53° (116) (note close proximity of this m.p. to that of the initial  $\bar{C}$ ).]

[ $\bar{C}$  on dinitration, e.g., with 4 wt. pts. fuming  $HNO_3$  ( $D = 1.62$ ) + 10 wt. pts. conc.  $H_2SO_4$  at b.p. for 5 hrs. (8) (121), or with 3 wt. pts.  $HNO_3$  ( $D = 1.52$ ) + 7.5 wt. pts. conc.  $H_2SO_4$  at b.p. for 2 hrs. (122), finally poured into aq., gives a mixt. contg. all three possible dinitro-*p*-dichlorobenzenes; of these the chief prod. is 1,4-dichloro-2,6-dinitrobenzene [Beil. V-265, V-(138)], m.p. 106° (123) (119), 105–106° (122), 105° (121), obtd. by recrystn if necessary) of the crude dinitration prod. from 30 r<sup>s</sup> (121); the contain the more soluble 1,4-dichloro-2,3-dinitro-

## 3:9912 n-HEXADECANOYL CHLORIDE

(Palmitoyl chloride)



Beil. II - 374

II<sub>1</sub>-(167)II<sub>2</sub>-(341)

B.P. 190-200° at	20 mm. (1)	M.P. 12° (5) (14)
194-195° at	17 mm. (2)	
198-200° at	15 mm. (3)	
192-199° at	15 mm. (4)	
192.5° at	15 mm. (5)	
191-194° at	14-15 mm. (6)	
183-185° at	11 mm. (7)	
172° at	5 mm. (8)	
139-140° at	1 mm. (35)	
162-163° at	0.8 mm. (9)	
145-152° at	0.45 mm. (45)	
143° at	0.3 mm. (10)	
155-190° at	0.2 mm. (11)	

Note that care must be taken to avoid confusion of  $\bar{\text{C}}$  with palmityl chloride (1-chlorohexadecane) (3:0015).

PREPARATION OF  $\bar{\text{C}}$ 

[For prepn. of  $\bar{\text{C}}$  from palmitic acid (1:0650) with  $\text{PCl}_5$  (yields: 60% (2), 49% (12)) (5) (13) (14) (15) (16), with  $\text{PCl}_5 + \text{ZnCl}_2$  (72% yield (12)), with  $\text{SOCl}_2$  directly (yields: 93.5% (7), 80% (12), 80% (0)) (17) (19) (45) or in  $\text{CCl}_4$  soln. (18), or with phosgene (3:5000) at 140-155° (70-75% yield (20)) see indic. refs.)

CHEMICAL BEHAVIOR OF  $\bar{\text{C}}$ 

## BEHAVIOR WITH INORGANIC REACTANTS

With sodium. [ $\bar{\text{C}}$  (1 mole) with metallic sodium (1.2 moles) in dry ether refluxed with stirring as directed gives (79% yield (6)) dotriaconten-16-diol-16,17 dipalmitate, i.e., the dipalmitate ester of  $\text{C}_{11}\text{H}_2(\text{CH}_2)_{14}\text{C}(\text{OH})=\text{C}(\text{OH})(\text{CH}_2)_{14}\text{CH}_3$ , cryst. from acetone/ $\text{C}_6\text{H}_6$  (3:1), m.p. 61-62° (6).]

With sodium azide. [ $\bar{\text{C}}$  with  $\text{NaN}_3$  in  $\text{C}_6\text{H}_6$  gives (14) palmitoyl azide [Beil. II-375] (not isolated by (14)) which loses  $\text{N}_2$  with rearr. to pentadecyl isocyanate [Beil. IV-202] (not isolated by (14) but from indirect prepn. reported (21) as m.p. 8-14° [cf. corresp. behavior of lauroyl chloride (3:9858)].]

With water.  $\bar{\text{C}}$  with aq. hydrolyzes to palmitic acid (1:0650) +  $\text{HCl}$ . [For study of rate of hydrolysis with ord.  $\text{H}_2\text{O}$  and with  $\text{D}_2\text{O}$  see (22).]

## BEHAVIOR WITH ORGANIC REACTANTS

With hydrocarbons. [ $\bar{\text{C}}$  with  $\text{C}_6\text{H}_6$  +  $\text{AlCl}_3$  gives (60% yield (23)) (21) (25) pentadecyl phenyl ketone (penmitophenone) [Beil. VII-347, VII<sub>1</sub>-(186)], lfts. from alc., m.p. 59° (23) (24) (26), b.p. 250.5-251.0° at 15 mm. (24) (corresp. oxime, m.p. 73-74° (26)). —  $\bar{\text{C}}$  with toluene +  $\text{AlCl}_3$  gives (24) pentadecyl p-tolyl ketone [Beil. VII-347, VII<sub>1</sub>-(186)], lfts. from alc., m.p. 60° (24) (26), b.p. 262° cor. at 15 mm. (24) (corresp. oxime, m.p. 60° (27), semicarbazone, m.p. 114.5° (26), phenylhydrazone, m.p. 54-55° (26)). — For analogous behavior of  $\bar{\text{C}}$  +  $\text{AlCl}_3$  + m-xylene (24), mesitylene (27) (2), diphenyl ether (28), and carbazole (28) see indic. refs.; for use of these products as waxes, addition agents for lubricants, etc., see (28) (29).]



With alcohols.  $\bar{C}$  with alcohols gives in general the corresp. alkyl palmitates [e.g.,  $\bar{C}$  with MeOH gives methyl palmitate (1:2055), m.p. 30°;  $\bar{C}$  with EtOH gives ethyl palmitate (1:2034),  $\alpha$ -form, m.p. 19.4°,  $\beta$ -form, m.p. 24.2°, etc.;  $\bar{C}$  with heptyl alc. (1:6480) gives (30) benzyl palmitate, m.p. 35°;  $\bar{C}$  with menthol (1:5940) gives (31) menthyl palmitate, m.p. 32°].

$\bar{C}$  (2 moles) with dihydric alcs. on htg. gives the corresp. neutral esters [e.g.,  $\bar{C}$  with ethylene glycol (1:6465) gives (32) ethylene glycol dipalmitate (1:2269), m.p. 70.5°;  $\bar{C}$  with propanediol-1,2 (1:6455) gives (32) propylene glycol dipalmitate, m.p. 52.5–54.5°;  $\bar{C}$  with butanediol-1,3 (1:6482) gives (32) 1,3-butylene glycol dipalmitate, m.p. 39–40°;  $\bar{C}$  with hutenediol-1,4 (1:6515) gives (32) tetramethylene glycol dipalmitate, m.p. 63°].

$\bar{C}$  has also been much employed in the prepn. of mixed glycerides, hut this topic cannot be expanded in detail in this text.

With phenols.  $\bar{C}$  on htg. with phenols splits out HCl yielding the corresp. esters. [E.g.,  $\bar{C}$  with phenol (1:1420) gives (5) phenyl palmitate, m.p. 45° (5), 44.5–46.0° (33), b.p. 249.5° at 15 mm. (5);  $\bar{C}$  with *p*-cresol (1:1410) gives (5) *p*-tolyl palmitate, m.p. 47°, b.p. 258° at 15 mm. —  $\bar{C}$  (2 moles) with pyrocatechol (1:1520) at 110° for 2 hrs gives (34) pyrocatechol dipalmitate, m.p. 58°;  $\bar{C}$  (2 moles) with resorcinol (1:1530) at 110° for 2 hrs. gives (34) resorcinol dipalmitate, m.p. 62.5–63.5°;  $\bar{C}$  (2 moles) with hydroquinone (1:1590) at 110° for 2 hrs. gives (34) hydroquinone dipalmitate, m.p. 94.5°].

[ $\bar{C}$  with phenol (1:1420) +  $AlCl_3$  in *sym*-tetrachloroethane (3:6750) as solvent, however, gives (35) (33) (36) a mixt. of the corresp. hydroxypalmitophenones; viz., 25.4% yield *o*-hydroxyphenyl pentadecyl ketone, m.p. 54–55° (corresp. 2,4-dinitrophenylhydrazone, m.p. 94–95° (35)), and 28.5% yield *p*-hydroxyphenyl pentadecyl ketone, m.p. 84.5–85° (35), 78° (37) (corresp. 2,4-dinitrophenylhydrazone, m.p. 141–142° (35)); for study of influence upon *o/p* ratio of use of nitrobenzene and of  $CS_2$  as solvents see (36).]

With salts of organic acids. [ $\bar{C}$  with Ag palmitate at 100° for 10 min. (38) or  $\bar{C}$  with  $Na\bar{A}$  (32) (42) gives palmitic anhydride (1:0651), m.p. 64° (39), 63.9° (40), 63–64° (41), 63° (38), 62–63° (32) (43), hut the latter is usually prepd. from palmitic acid (1:0650) by htg. with  $Ac_2O$  (39) (40) (41) (42) (43).]

With esters. [ $\bar{C}$  with diethyl sodiomalonate would be expected to give diethyl palmitoylmalonate, hut for unsuccessful attempt to realize this reaction see (44).]

[ $\bar{C}$  with ethyl sodio-acetoacetate in dry ether gives (62% yield (11)) (45) ethyl  $\alpha$ -palmitoylacetoacetate, m.p. 36–36.5° (11) (45); note that this prod. with aq. NaOH splits off the acetyl group giving (52% yield (11)) ethyl palmitoylacetae, m.p. 37–38° (11) (45).]

With amines.  $\bar{C}$  with org. prim. amines yields the corresp. amides [e.g.,  $\bar{C}$  with *p*-cymidine (2-methyl-5-isopropylaniline) gives (1) palmito-(2-methyl-5-isopropyl)anilide, m.p. 90–91°;  $\bar{C}$  with vanillylamine (4-hydroxy-3-methoxybenzylamine) gives (8) *N*-(vanillyl)-palmitamide,  $\alpha$ -form, m.p. 89–89.5°,  $\beta$ -form, m.p. 84–84.5°].

$\bar{C}$  on hydrolysis yields palmitic acid (1:0650), m.p. 62.7°; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see palmitic acid (1:0650).

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(31) I<sup>1</sup> 733-742

*Atti ut.* (1910).

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— 1-CHLOROHEPTADECANE  $\text{CH}_3(\text{CH}_2)_{15}\text{CH}_2\text{Cl}$   $\text{C}_{17}\text{H}_{35}\text{Cl}$  Beil. I —  
(*n*-Heptadecyl chloride)  $\text{I}_1$ -(60)  
 $\text{I}_2$ —

B.P. 192-195° at 10 mm. M.P. 24°

See 3:0100. Division A: Solids.

3:9925 *n*-HEPTADECANOYL CHLORIDE  $\text{C}_{17}\text{H}_{33}\text{OCl}$  Beil. S.N. 102  
(*n*-Margaroyl chloride)  $\text{CH}_3(\text{CH}_2)_{15}-\text{C}=\text{O}$   
 $\text{Cl}$

B.P. 176° at 4 mm. (1)  
139-144° at 0.04 mm. (2)

[For prepn. of  $\bar{C}$  from margaric acid (1:0635) with  $\text{SOCl}_2$  (84.5% yield (2)) (1) (3) see indie. refs.]

$\bar{C}$  with phenol (1:1420) on litg. gives (3) phenyl margarate, cryst. from MeOH, m.p. 37°, b.p. 210-250° dec. at 11 mm. (3).

[ $\bar{C}$  with alkali margarates presumably would yield margaric anhydride, cryst. from ether or pet. ether, in p. 67.6° cor. (1), although this reaction has not actually been reported and the margaric anhydride is readily obtd. from the acid (1:0635) with  $\text{Ac}_2\text{O}$  (1).]

[For reaction of  $\bar{C}$  with vanillylamine see (1); with 1,7-aminonaphthol see (2).]

$\bar{C}$  on hydrolysis yields margaric acid (1:0635); for the amide and other derivs. corresp. to  $\bar{C}$  see margaric acid (1:0635).

3:9925 (1) Ford-Moore, Phillips, *Rer. trav. chim.* 53, 558 (1931). (2) Fierz-David, Kuster, *Helv. Chim. Acta* 22, 59, 101 (1939). (3) Skraup, Schwamberger, *Ann.* 462, 153 (1925). (4) Wallace, Copenhagen, *J. Am. Chem. Soc.* 63, 699-700 (1911).

— 1-CHLORO-OCTADECANE  $\text{CH}_3(\text{CH}_2)_{17}\text{CH}_2\text{Cl}$   $\text{C}_{19}\text{H}_{39}\text{Cl}$  Beil. S.N. 10  
(*n*-Octadecyl chloride;  
stearyl chloride)

B.P. 180-190° at 12 mm. M.P. 21°

See 3:0095. Division A: Solids



[For prepn. of  $\bar{C}$  from elaidic acid (1:0610) with  $PCl_5$  (1), with  $SOCl_2$  (2), or with oxalyl (di)chloride (3:5060) (91% yield (5)) cf. (6) see indic. refs.]  
[For reactn. of  $\bar{C}$  with diazomethane giving (83% yield (2)) 1-diazononadecen-10-one-2, m.p. 53° (2), see (2); for reactn. of  $\bar{C}$  with ethyl sodio-acetosuccinate see (3); for use of  $\bar{C}$  in prepn. of synthetic glycerides see (4).]  
 $\bar{C}$  on hydrolysis yields elaidic acid (1:0610) (for the amide and other derivatives corresp. to  $\bar{C}$  see 1:0610).

3:9950 (1) Kraftt, Tritschler, *Ber.* 33, 3582 (1900). (2) Grundmann, *Ann.* 524, 43 (1936). (3) Robinson, *J. Chem. Soc.* 1930, 750. (4) Böhmer, Kappeller, *Fette u. Seifen* 44, 340-343 (1937); *Cent.* 1939, 1 573. (5) Daubert, *J. Am. Chem. Soc.* 66, 291 (1944). (6) Wood, Jackson, Baldwin, Longenecker, *J. Am. Chem. Soc.* 66, 287-289 (1944).

3:9960

$n$ -OCTADECANOYL CHLORIDE

(Stearoyl chloride)

$CH_3(CH_2)_{16}-C(=O)Cl$

$C_{18}H_{35}OCl$

Beil. II - 384

$II_1$ -(170)

$II_2$ -(360)

B.P. 215°	at	15 mm.	(1)	M.P. 24°	(2)
211-210°	at	15 mm.	(2)	23°	(1)
200-215°	at	13-15 mm.	(3)	23.2-23.4°	(8)
205°	at	9 mm.	(4)		
202-203°	at	6 mm.	(5)		
180-100°	at	5-6 mm.	(15)		
203°	at	5 mm.	(6)		
185°	at	3 mm.	(7)		
195-195.5°	at	2 mm.	(8)		
164-100°	at	0.5-1.0 mm.	(9)		
176-178°	at	0.5 mm.	(10)		
165°	at	0.4 mm.	(11)		

Note that care must be taken to avoid confusion of  $\bar{C}$  with stearyl chloride (1-chlorooctadecane) (3:0035).

PREPARATION OF  $\bar{C}$

[For prepn. of  $\bar{C}$  from stearic acid (1:0660) with  $PCl_5$  directly (1) (12) (13) (21) or in  $CCl_4$  soln. (14), with  $SOCl_2$  directly (yields: 97% (10), 81% (3)) (4) (7) (15) (16) (17) or in  $CCl_4$  soln. (yield 80% (8)) (14), with  $PCl_5$  (15), with oxalyl (di)chloride (3:5060) (11), or with phosgene (3:5000) at 140-150° (70-75% yield (19)) see indic. refs.]

CHEMICAL BEHAVIOR OF  $\bar{C}$

BEHAVIOR WITH INORGANIC REAGENTS

Hydrogenation of  $\bar{C}$ . [ $\bar{C}$  with  $H_2$  +  $Pd/BaSO_4$  cat. in boilg. xylene gives (20) (21) stearaldehyde (1:0012).]  
Behavior with bromine. [For behavior of  $\bar{C}$  with  $Br_2$  at room temp., 100°, and 135° see (22).]  
Behavior with sodium. [ $\bar{C}$  (1 mole) with metallic sodium (1.2 moles) in dry ether under reflux gives (67% yield (3)) hexatriaconten-18-diol-18,10 distearate, i.e., the distearate ester of  $CH_3(CH_2)_{16}C(OH)=C(OH)(CH_2)_{16}CH_3$ , m.p. 67-68°.]  
With sodium azide. [ $\bar{C}$  with  $NaN_3$  in  $C_6H_6$  gives (23) (12) stearyl azide (not isolated) which loses  $N_2$  with rearr. giving (43% yield (23)) heptadecyl isocyanate, b.p. 206-209°

at 17 mm. {23}, 200-203° at 15 mm. {24}; cf. the corresp. behavior of lauroyl chloride (3:9858).]

With water.  $\bar{C}$  with aq. hydrolyzes to stearic acid (1:0660) + HCl.

#### BEHAVIOR WITH ORGANIC REACTANTS

With hydrocarbons (or their equivalents). [ $\bar{C}$  with  $C_6H_6$  +  $AlCl_3$  gives (yields: 65% {25}, 60% {26}) {27} {18} heptadecyl phenyl ketone (stearophenone) (Beil. VII-347, VII-1-(187)), lfts. from alc., m.p. 64-65° {25}, 63.5-64.5° {18}, 64° {28}, 59° {27} {29} (corresp. oxime, m.p. 53° {27}, phenylhydrazone, m.p. 54° {28}); note that in this reaction no introduction of a second acyl radical occurs {30}, and that attempts to prepare stearophenone by use (with  $C_6H_6$  +  $AlCl_3$ ) of the mixed anhydride from stearic acid with ketene) gave very poor yields {29}. — For patents on the use of stearophenone as an electric insulator {31}, on its sulfonation {32}, or on its reaction with  $PCl_3$  {33} see indic. refs.]

[ $\bar{C}$  with toluene +  $AlCl_3$  gives {34} heptadecyl *p*-tolyl-ketone (Beil. VII-347, VII-1-(187)), lfts. from alc., m.p. 67° {34}, 66-67° {28}, b.p. 278° cor. at 15 mm. {34} (corresp. oxime, m.p. 64° {27}). — For analogous behavior of  $\bar{C}$  with naphthalene (1:7200) {18}, tetralin (1:7550) {18}, biphenyl (1:7175) {18} {35}, *p*-methylbiphenyl {35}, *p*-chlorobiphenyl (3:1912) {35}, diphenyl ether (1:7125) {35}, *p*-nitrodiphenyl ether {35}, furan (1:8015) {35}, 2-methylfuran {35}, dibenzofuran {35}, thiophene {35}, dibenzothiophene {35}, carbazole {35}, etc., see indic. refs.; for use of these products as waxes, addition agents for lubricants, etc., see {35} {36}.]

[For behavior of  $\bar{C}$  with resins derived from indene, coumarone, or dicyclopentadiene see {37}. — For addition of  $\bar{C}$  to alkynes in pres. of a condensing agent such as  $AlCl_3$ ,  $ZnCl_2$ , etc., see {38} cf. {39}.]

With alcohols.  $\bar{C}$  with alcohols gives in general the corresp. alkyl stearates. [E.g.,  $\bar{C}$  with MeOH gives methyl stearate (1:2095), m.p. 33.8°;  $\bar{C}$  with EtOH gives ethyl stearate (1:2078),  $\alpha$ -form, m.p. 30.0°,  $\beta$ -form, m.p. 33.5°. —  $\bar{C}$  with benzyl alc. (1:6480) gives {40} benzyl stearate, m.p. 45.8°;  $\bar{C}$  with menthol (1:5940) gives {41} menthyl stearate, m.p. 38-39°.]

$\bar{C}$  has also been much employed in the prepn. of mixed glycerides, but this topic cannot be expanded in detail in this text.

With phenols. [ $\bar{C}$  on hgt. with phenols splits out HCl yielding the corresp. esters: e.g.,  $\bar{C}$  with phenol (1:1420) gives {1} phenyl stearate, m.p. 52° {1}, 61.5-53.0 {44}, b.p. 267° at 15 mm. {1};  $\bar{C}$  with *p*-cresol (1:1410) gives {1} *p*-tolyl stearate, m.p. 64°, b.p. 276° at 16 mm.]

[ $\bar{C}$  (2 moles) with pyrocatechol (1:1520) at 100° gives {42} {43} pyrocatechol distearate, m.p. 83-85° {43}, 68° {42};  $\bar{C}$  (2 moles) with hydroquinone (1:1590) at 130° gives {42} hydroquinone distearate, m.p. 97°.]

[ $\bar{C}$  with phenol (1:1420) +  $AlCl_3$  in *sym*-tetrachloroethane (3:6750) as solvent, however, gives {45} {44} {46} a mixt. of the corresp. hydroxystearophenones: viz., 27.8% yield *o*-hydroxyphenyl heptadecyl ketone, m.p. 64-66° (corresp. 2,4-dinitrophenylhydrazone, m.p. 96-97° {45}); and 28% yield *p*-hydroxyphenyl heptadecyl ketone, m.p. 87-89° corresp. 2,4-dinitrophenylhydrazone, m.p. 139.5-140° {45}); for study of influence upon *o/p* ratio of use of nitrobenzene or of  $CS_2$  as solvents see {46}.]

With salts of organic acids. [ $\bar{C}$  with Ag stearate at 100° for 10 min. gives {47} stearic nnhydride (1:4915), m.p. 71-72° {48}, 71-71.5° {49}, 70.7° {50}, 70.5° {47}, 70-71° {51}, but the latter is usually prepd. from stearic acid (1:0660) by hgt. with  $Ac_2O$  {48} {49} {50} {51}.]

With esters.  $\bar{C}$  with ethyl sodio-acetoacetate refluxed 1 hr. under  $N_2$  gives (68% yield (52)) ethyl  $\alpha$ -stearoylacetate, m.p. 42°; note that this prod. with aq. NaOH splits off its acetyl group giving (74% yield (52)) ethyl stearoylacetate, m.p. 46.5° (corresp. copper enolate, m.p. 111–112°).]

With Grignard reagents.  $\bar{C}$  with *ter*-BuMgBr gives (28.5% yield (8)) *ter*-butyl *n*-heptadecyl ketone, m.p. 44.8–45.1° (corresp. semicarbazone, m.p. 78.0–78.2°); note that low yield suggests probability that the RMgBr also acted as a reducing agent cf. corresp. behavior of lauroyl chloride (3:9858), but no study of such effect for this combination is reported. —  $\bar{C}$  with cyclohexyl MgBr gives (8) cyclohexyl *n*-heptadecyl ketone.]

$\bar{C}$  with EtMgBr + CdCl<sub>2</sub> (53) or  $\bar{C}$  with ZnEt<sub>2</sub> (54) gives (65% yield (53)) ethyl *n*-heptadecyl ketone (eikosanone-3) [Beil. I-719, I<sub>1</sub>-(374), I<sub>2</sub>-(774)], m.p. 60–61° (54), 59.5–60° (55), 57° (28), 54–55° (53) (corresp. oxime, m.p. 55.5–56.5° (54), semicarbazone, m.p. 89–91° (53))]

With diazomethane.  $\bar{C}$  with CH<sub>2</sub>N<sub>2</sub> (2.2 moles) as directed gives (88.5% yield (15)) 1-diazononadecanone-2, m.p. 69°, which in AcOH loses N<sub>2</sub> and esterifies giving (89% yield (15)) nonadecanone-2-yl-1 acetate, m.p. 72°.]

With amines.  $\bar{C}$  with org. prim. amines yields the corresp. amides [e.g.,  $\bar{C}$  with *p*-cymidine (2-methyl-5-isopropylaniline) gives (56) stearo-(2-methyl-5-isopropyl)anilide, m.p. 93–94°;  $\bar{C}$  with vanillylamine (4-hydroxy-3-methoxybenzylamine) gives (5) *N*-(vanillyl)-stearamide,  $\alpha$ -form, m.p. 94.5–95°,  $\beta$ -form, m.p. 90.0–90.5°].

$\bar{C}$  on hydrolysis yields stearic acid (1:0660), m.p. 69–70°; for the amide, anilide, *p*-toluidide, and other derivatives corresp. to  $\bar{C}$  see stearic acid (1:0660).

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## CHAPTER XXIII

### I. INDEX OF COMPOUNDS ACCORDING TO EMPIRICAL FORMULA

This Empirical Formula Index comprises four parts as follows:

- A. Compounds containing only carbon and chlorine.
- B. Compounds containing only carbon, oxygen, and chlorine.
- C. Compounds containing only carbon, hydrogen, and chlorine.
- D. Compounds containing only carbon, hydrogen, oxygen, and chlorine.

Within each section the component individuals are arranged in groups according to increasing number of carbon atoms. Within each group of isomeric compounds the order of listing follows the sequence of the eight units comprising the Chemical Type Index.

#### A. COMPOUNDS CONTAINING ONLY CARBON AND CHLORINE

<b>C<sub>1</sub> GROUP</b>			<b>C<sub>4</sub> GROUP</b>		
CCl <sub>4</sub>	M.W. = 153.8	Cl = 92.2%	C <sub>4</sub> Cl <sub>2</sub>	M.W. = 119.0	Cl = 59.6%
Carbon tetrachloride		3:5109	1,4-Dichlorobutadiene-1,3		3:9040
<b>C<sub>2</sub> GROUP</b>			<b>C<sub>5</sub> GROUP</b>		
C <sub>2</sub> Cl <sub>2</sub>	M.W. = 91.9	Cl = 74.7%	C <sub>5</sub> Cl <sub>4</sub>	M.W. = 260.8	Cl = 81.6%
Dichloroacetylene		3:5010	Hexachlorobutadiene-1,3		3:6425
C <sub>3</sub> Cl <sub>4</sub>	M.W. = 165.8	Cl = 85.5%	C <sub>5</sub> Cl <sub>3</sub>	M.W. = 343.7	Cl = 82.5%
Tetrachloroethylene		3:5460	Octachlorocyclopentene		3:0422
C <sub>3</sub> Cl <sub>6</sub>	M.W. = 236.8	Cl = 89.9%	<b>C<sub>6</sub> GROUP</b>		
Hexachloroethane		3:4835	C <sub>6</sub> Cl <sub>4</sub>	M.W. = 284.8	Cl = 74.7%
<b>C<sub>3</sub> GROUP</b>			Hexachlorobenzene		3:4939
C <sub>3</sub> Cl <sub>4</sub>	M.W. = 218.8	Cl = 85.5%	<b>C<sub>10</sub> GROUP</b>		
Hexachloropropene		3:6370	C <sub>10</sub> Cl <sub>8</sub>	M.W. = 403.8	Cl = 70.3%
C <sub>4</sub> Cl <sub>6</sub>	M.W. = 310.7	Cl = 88.7%	Octachloronaphthalene		3:4893
Octachloropropane		3:4450			

#### B. COMPOUNDS CONTAINING ONLY CARBON, OXYGEN, AND CHLORINE

<b>C<sub>1</sub> GROUP</b>			<b>C<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub></b>		
COCl <sub>2</sub>	M.W. = 98.9	Cl = 71.7%	Oxalyl (di)chloride	M.W. = 126.9	Cl = 55.9%
Carbonyl chloride (phosgene)		3:5000			3:5060
<b>C<sub>2</sub> GROUP</b>			<b>C<sub>3</sub>O<sub>2</sub>Cl<sub>4</sub></b>		
C <sub>2</sub> OCl <sub>4</sub>	M.W. = 181.8	Cl = 78.0%	Trichloromethyl chloroformate (diphosgene)	M.W. = 197.8	Cl = 71.7%
Trichloroacetyl chloride		3:5470			3:5315



**C<sub>3</sub> GROUP**  
 $C_3OCl_4$  M.W. = 193.9 Cl = 73.2%  
 Trichloroacryloyl chloride 3:5845

$C_3OCl_6$  M.W. = 124.1 Cl = 58.1%  
 Hexachloroacetone 3:6312  
 Pentachloropropionyl chloride 3:0470

$C_3O_2Cl_6$  M.W. = 280.8 Cl = 75.8%  
 Trichloromethyl trichloroacetate 3:0290

$C_3O_3Cl_6$  M.W. = 296.8 Cl = 71.7%  
 Di-(trichloromethyl)  
 carbonate (triphosgene) 3:1915

**C<sub>4</sub> GROUP**  
 $C_4OCl_6$  M.W. = 276.8 Cl = 75.9%  
 Di-(trichlorovinyl) ether 3:6373

$C_4OCl_{10}$  M.W. = 418.5 Cl = 84.7%  
 Decachlorodiethyl ether 3:1676

$C_4O_2Cl_4$  M.W. = 221.9 Cl = 63.9%  
 Dichloromalacyl (di)chloride 3:6197

$C_4O_3Cl_2$  M.W. = 167.0 Cl = 42.5%  
 Dichloromaleic anhydride 3:3635

$C_4O_2Cl_6$  M.W. = 308.8 Cl = 68.9%  
 Trichloroacetic acid anhydride 3:6575

**C<sub>6</sub> GROUP**  
 $C_6OCl_4$  M.W. = 300.8 Cl = 70.0%  
 "Hexachlorophenol" 3:3180

$C_6O_2Cl_4$  M.W. = 245.9 Cl = 57.7%  
 Tetrachlorobenzoquinone-1,2 3:3963  
 Tetrachlorobenzoquinone-1,4  
 (chloranil) 3:4978

$C_6O_2Cl_6$  M.W. = 316.8 Cl = 57.2%  
 2,3,5,5,6,6-Hexachloro-  
 cyclohexen-2-dione-1,4 3:3260  
 "Hexachlororesorcinol" 3:3470

**C<sub>7</sub> GROUP**  
 $C_7OCl_5$  M.W. = 312.8 Cl = 68.0%  
 Pentachlorobenzoyl chloride 3:2295

**C<sub>8</sub> GROUP**  
 $C_8O_3Cl_4$  M.W. = 285.9 Cl = 49.6%  
 Tetrachlorophthalic anhydride 3:4947

### C. COMPOUNDS CONTAINING ONLY CARBON, HYDROGEN, AND CHLORIDE

**C<sub>1</sub> GROUP**  
 $CHCl_3$  M.W. = 119.4 Cl = 89.1%  
 Chloroform 3:5050

$CH_2Cl_2$  M.W. = 84.0 Cl = 83.5%  
 Methylene (di)chloride 3:5020

$CH_3Cl$  M.W. = 50.5 Cl = 70.2%  
 Methyl chloride 3:7005

**C<sub>2</sub> GROUP**  
 $C_2HCl$  M.W. = 60.5 Cl = 58.6%  
 Chloroacetylene 3:7000

$C_2HCl_3$  M.W. = 131.4 Cl = 81.0%  
 Trichloroethylene 3:5170

$C_2HCl_5$  M.W. = 202.3 Cl = 87.6%  
 Pentachloroethane 3:5880

$C_2H_2Cl_2$  M.W. = 97.0 Cl = 73.1%  
 1,1-Dichloroethylene 3:5005  
 (vinylidene (di)chloride) 3:5042  
 1,2-Dichloroethylene (*cis* form) 3:5023  
 1,2-Dichloroethylene (*trans* form) 3:5030  
 1,2-Dichloroethylene (ord. mixt.) 3:5030

$C_2H_2Cl_4$  M.W. = 167.9 Cl = 81.5%  
 1,1,1,2-Tetrachloroethane 3:5555  
 1,1,2,2-Tetrachloroethane 3:5750

$C_2H_3Cl$  M.W. = 62.5 Cl = 56.7%  
 Vinyl chloride 3:7010

$C_2H_3Cl_3$  M.W. = 133.4 Cl = 79.7%  
 1,1,1-Trichloroethane 3:5085  
 1,1,2-Trichloroethane 3:5330

$C_2H_4Cl_2$  M.W. = 99.0 Cl = 71.7%  
 1,1-Dichloroethane 3:5035  
 1,2-Dichloroethane 3:5130

$C_2H_5Cl$  M.W. = 64.5 Cl = 55.1%  
 Ethyl chloride 3:7015

**C<sub>3</sub> GROUP**  
 $C_3HCl_3$  M.W. = 214.3 Cl = 82.7%  
 1,1,2,3,3-Pentachloropropene-1 3:6075

$C_3HCl_7$  M.W. = 285.2 Cl = 87.0%  
 1,1,1,2,2,3,3-Heptachloropropane 3:0200  
 1,1,1,2,3,3,3-Heptachloropropane 3:6560

$C_3H_2Cl_4$  M.W. = 179.9 Cl = 78.8%  
 1,2,3,3-Tetrachloropropene-1 3:5920

$C_3H_2Cl_6$  M.W. = 250.8 Cl = 84.8%  
 1,1,1,2,3,3-Hexachloropropane 3:6460  
 1,1,2,2,3,3-Hexachloropropane 3:6525

$C_3H_3Cl$  M.W. = 74.5 Cl = 47.6%  
 3-Chloropropyne-1 3:7100

101° (121), and 1,4-dichloro-2,5-dinitrobenzene, m.p. 119° (122) (121) (124). — For f.p. compn. data and diagrams of mixtures of the 2,6- and 2,3-dinitro-*p*-dichlorobenzenes see (119), of mixtures of the 2,6- and 2,5-dinitro-*p*-dichlorobenzenes see (121). — Note also that the prod., m.p. 81°, formerly (8) supposed to be the 2,5-dinitro isomer, has since (121) been proved to be a compound of the 2,6- and 2,5-dinitro-1,4-dichlorobenzenes. — The relative proportion of the three dinitration products varies with conditions (119) (121) (122) (124).]

[ $\bar{C}$  on monosulfonation, e.g., with 1.5 wt. pts. fuming  $H_2SO_4$  (10–12%  $SO_3$ ) at 140–150° for 45 min. (118) cf. (27), gives on pouring into aq. (85–90% yield (118)) 1,4-dichlorobenzene-sulfonic acid-2, cryst. from aq. as monohydrate (for derivs. see below). — Note that  $\bar{C}$  is not sulfonated by conc.  $H_2SO_4$  even at 210° (16) (dif. from *o*-dichlorobenzene (3:6055) and use in sepn. from  $\bar{C}$ ); for removal of chlorobenzene (3:7903) from mixt. with dichlorobenzenes via sulfonation of former with 95%  $H_2SO_4$  see (17). — For use of reactn. prod. of  $\bar{C}$  with  $SO_2$  as dye intermed. or for mothproofing of wool see (125). — For reactn. of sodium *p*-dichlorobenzene-sulfonate with fused  $NaOH$  to yield hydroquinone (1:1590) see (126).]

[ $\bar{C}$  with 5 moles  $ClSO_3H$  at 150° for 1 hr. (127) (128) gives (85% yield (127) (128)) 1,4-dichlorobenzene-sulfonyl chloride-2, cryst. from lgr., m.p. 39° (127) (128), 38° (129), 36.8° (27) (corresp. amide, see below; corresp. sulfonanilide, m.p. 160° (128)); for use in prepn. of tetrachlorothioindigo see (130). —  $\bar{C}$  with 30 pts.  $ClSO_3H$  at 140° for 48 hrs. (128) gives both 1,4-dichlorobenzene-*bis*-(sulfonyl chloride)-2,6, m.p. 114° (corresp. *bis*-sulfonanilide, m.p. 215–217° dec (128)) and 1,4-dichlorobenzene-*bis*-(sulfonyl chloride)-2,5, m.p. 162° (corresp. *bis*-sulfonanilide, m.p. not given). — Note that  $\bar{C}$  reacts with  $ClSO_3H$  much less easily than *o*-dichlorobenzene; for use in sepn. of the two isomers via formn. of *o*-dichlorobenzene-sulfonyl chloride and sepn. from unchanged  $\bar{C}$  by distn. see (131).]

④ 1,4-Dichlorobenzene-sulfonamide-2 (2,5-dichlorobenzene-sulfonamide-1): cryst. from dil. alc., m.p. 179.5–180° u.c. (129), 181° (127), 185–186° (27) [From  $\bar{C}$  via treatment with  $ClSO_3H$  as directed (129) to 1,4-dichlorobenzene-sulfonyl chloride-2 (see above) and subsequent conv. with  $(NH_4)_2CO_3$  to desired sulfonamide] — [Note that, although the m.p. of this sulfonamide is practically identical with that from *m*-dichlorobenzene (3:5960), each depresses the m.p. of a mixt. with the other; the m.p.'s of the precursor sulfonyl chlorides, viz. 52–53° for the isomer from *m*-dichlorobenzene, 38° for that from  $\bar{C}$ , may also serve to distinguish them (129).] — [For similar prepn. and use of 1,4-dichlorobenzene-sulfonamide-2 see (132).]

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2,3-Dichlorobutene-2		$C_4H_6Cl$	M.W. = 92.6	Cl = 33.3%
Higher-boiling isomer ( <i>trans</i> )	3:7395	1-Chlorobutane		3:7160
Lower-boiling isomer ( <i>cis</i> )	3:5500	2-Chlorobutane		3:7125
1,1-Dichloro-2-methylpropene-1		1-Chloro-2-methylpropene		3:7135
1,3-Dichloro-2-methylpropene-1	3:5590	2-Chloro-2-methylpropene		3:7045
3,3-Dichloro-2-methylpropene-1	3:7480	$C_5$ GROUP		
3-Chloro-2-(chloromethyl)-propene-1	3:5633	$C_5H_8Cl_2$	M.W. = 137.0	Cl = 51.8%
$C_4H_8Cl_4$	M.W. = 195.9	1-Chloro-2-(chloromethyl)-butadiene-1,3		3:9195
1,1,1,2-Tetrachlorobutane	3:5622	$C_6H_7Cl$	M.W. = 102.6	Cl = 34.6%
1,2,2,3-Tetrachlorobutane	3:9078	1-Chloro-3-methylbutadiene-1,2		3:7390
1,2,3,3-Tetrachlorobutane	3:9080	3-Chloropentadiene-1,3		3:7360
1,2,3,4-Tetrachlorobutane		1-Chloro-2-methylbutadiene-1,3		3:9200
Solid isomer	3:1750	3-Chloro-2-methylbutadiene-1,3		3:7290
Liquid isomer	3:9082	1-Chloro-3-methylbutadiene-1,3		3:7355
1,1,1,2-Tetrachloro-2-methylpropane	3:4725	3-Chloro-3-methylbutyne-1		3:7155
1,1,2,3-Tetrachloro-2-methylpropane	3:6165	$C_6H_7Cl_3$	M.W. = 173.5	Cl = 61.3%
1,1,3-Trichloro-2-(chloromethyl)propane	3:9084	1,3-Dichloro-2-(chloromethyl)butene-1		3:0201
1,2,3-Trichloro-2-(chloromethyl)propane	3:6335	$C_6H_7Cl_4$	M.W. = 244.4	Cl = 72.5%
$C_4H_7Cl$	M.W. = 90.6	3,3,4,4,4-Pentachloro-2-methylbutane		3:6725
1-Chlorobutene-1	3:7110	$C_6H_8Cl_2$	M.W. = 139.0	Cl = 51.0%
2-Chlorobutene-1	3:7075	2,5-Dichloropentene-2		3:9202
3-Chlorobutene-1	3:7090	3,4-Dichloropentene-2		3:8045
4-Chlorobutene-1	3:7151	3,3-Dichloro-2-methylbutene-1		3:7690
1-Chlorobutene-2	3:7205	3-Chloro-2-(chloromethyl)butene-1		3:9206
2-Chlorobutene-2	3:7105	1,3-Dichloro-2-methylbutene-2		3:8170
1-Chloro-2-methylpropene-1 (isocrotyl chloride)	3:7120	1,4-Dichloro-2-methylbutene-2		3:9204
3-Chloro-2-methylpropene-1 (methallyl chloride)	3:7145	$C_6H_8Cl_3$	M.W. = 209.9	Cl = 67.6%
$C_4H_7Cl_3$	M.W. = 161.5	1,2,3-Trichloro-2-(chloromethyl)butane		3:5230
1,1,3-Trichlorobutane	3:9086	1,3-Dichloro-2,2-bis-(chloromethyl)propane		3:2675
1,2,3-Trichlorobutane	3:5935	$C_6H_9Cl$	M.W. = 104.6	Cl = 33.9%
2,2,3-Trichlorobutane	3:5690	1-Chloropentene-1		3:7420
1,1,2-Trichloro-2-methylpropane	3:5710	2-Chloropentene-1		3:7280
1,2,3-Trichloro-2-methylpropane	3:5885	3-Chloropentene-1		3:7260
$C_4H_8Cl_2$	M.W. = 127.0	4-Chloropentene-1		3:7350
1,1-Dichlorobutane	3:7550	5-Chloropentene-1		3:7410
1,2-Dichlorobutane	3:7680	1-Chloropentene-2		3:7470
1,3-Dichlorobutane	3:7925	2-Chloropentene-2		3:7285
1,4-Dichlorobutane	3:5835	3-Chloropentene-2		3:7240
2,2-Dichlorobutane	3:7415	4-Chloropentene-2		3:7400
2,3-Dichlorobutane		5-Chloropentene-2		3:7455
<i>d,l</i> (racemic) isomer	3:7615	1-Chloro-2-methylbutene-1		3:7303
<i>meso</i> isomer	3:7580	2-(Chloromethyl)butene-1		3:9214
1,1-Dichloro-2-methylpropane	3:7425	3-Chloro-2-methylbutene-1		3:7300
1,2-Dichloro-2-methylpropane	3:7430			
1,3-Dichloro-2-methylpropane	3:7960			

$C_3H_3Cl_3$	M.W. = 145.4	Cl = 73.1%	$C_4H_2Cl_8$	M.W. = 333.8	Cl = 85.0%
1,1,2-Trichloropropene-1		3:5395	1,1,2,2,3,3,4,4-Octachlorobutane		3:2000
1,2,3-Trichloropropene-1		3:5650			
3,3,3-Trichloropropene-1		3:5345	$C_4H_2Cl$	M.W. = 86.5	Cl = 41.0%
			1-Chlorobuten-3-yne-1		3:7070
$C_4H_3Cl_5$	M.W. = 216.3	Cl = 82.0%	$C_4H_2Cl_3$	M.W. = 157.4	Cl = 67.6%
1,1,1,2,3-Pentachloropropene		3:4740	1,2,3-Trichlorobutadiene-1,3		3:9052
1,1,2,3,3-Pentachloropropene		3:6280			
$C_4H_2Cl_2$	M.W. = 111.0	Cl = 63.9%	$C_4H_2Cl_6$	M.W. = 228.4	Cl = 77.6%
1,1-Dichloropropene-1		3:5120	1,1,1,4,4-Pentachlorobutene-2		3:9054
1,2-Dichloropropene-1					
Higher-boiling isomer		3:5150	$C_4H_2Cl_7$	M.W. = 299.3	Cl = 82.9%
1,2-Dichloropropene-1			1,1,2,2,3,4,4-Heptachlorobutane		3:9056
Lower-boiling isomer		3:5110			
1,3-Dichloropropene-1		3:5280	$C_4H_2Cl_2$	M.W. = 123.0	Cl = 57.7%
2,3-Dichloropropene-1		3:5190	1,2-Dichlorobutadiene-1,3		3:9057
3,3-Dichloropropene-1		3:5140	2,3-Dichlorobutadiene-1,3		3:5220
$C_4H_4Cl_4$	M.W. = 181.9	Cl = 78.0%	$C_4H_2Cl_4$	M.W. = 193.9	Cl = 73.1%
1,1,1,2-Tetrachloropropene		3:5785	1,3,4,4-Tetrachlorobutene-1		3:9058
1,1,2,2-Tetrachloropropene		3:5825	2,3,3,4-Tetrachlorobutene-1		3:9060
1,1,2,3-Tetrachloropropene		3:6035			
1,2,2,3-Tetrachloropropene		3:5895	$C_4H_2Cl_5$	M.W. = 264.8	Cl = 80.3%
			1,1,2,3,4,4-Hexachlorobutane		3:3155
$C_4H_3Cl$	M.W. = 76.5	Cl = 46.3%			
1-Chloropropene-1		3:7030	$C_4H_2Cl$	M.W. = 88.5	Cl = 40.1%
2-Chloropropene-1		3:7020	4-Chlorobutadiene-1,2		3:7225
3-Chloropropene-1 (allyl chloride)		3:7035	1-Chlorobutadiene-1,3		3:7210
			2-Chlorobutadiene-1,3		3:7080
$C_2H_2Cl_3$	M.W. = 147.4	Cl = 72.1%	(Chloroprene)		
1,1,1-Trichloropropene		3:5270	1-Chlorobutyne-2		3:7175
1,1,2-Trichloropropene		3:5630			
1,1,3-Trichloropropene		3:5660	$C_4H_2Cl_3$	M.W. = 159.5	Cl = 66.7%
1,2,2-Trichloropropene		3:5475	1,2,4-Trichlorobutene-2		3:9062
1,2,3-Trichloropropene		3:5840	2,3,4-Trichlorobutene-2		3:9064
			1,1,3-Trichloro-2-methylpropene-1		3:5025
$C_2H_2Cl_2$	M.W. = 113.0	Cl = 62.8%	3,3,3-Trichloro-2-methylpropene-1		3:5605
1,1-Dichloropropene		3:7230	1,3-Dichloro-2-(chloromethyl)-propene-1		3:9066
1,2-Dichloropropane		3:5200			
1,3-Dichloropropane		3:5450	$C_4H_2Cl_5$	M.W. = 230.4	Cl = 77.0%
2,2-Dichloropropane		3:7140	1,1,2,3,4-Pentachlorobutane		
			Solid isomer		3:0750
$C_2H_2Cl$	M.W. = 78.5	Cl = 45.1%	Liquid isomer		3:9068
1-Chloropropene		3:7010	1,2,2,3,4-Pentachlorobutane		3:9070
2-Chloropropene		3:7025	1,1,1,2,3-Pentachloro-2-methylpropane		3:1265
			1,1,2,3-Tetrachloro-2-(chloromethyl)propane		3:9072
<b>C<sub>4</sub> GROUP</b>					
$C_4HCl_4$	M.W. = 220.3	Cl = 78.3%	$C_4H_2Cl_2$	M.W. = 125.0	Cl = 56.7%
1,1,2,3,4-Pentachlorobutadiene-1,3		3:9044	1,3-Dichlorobutene-1		3:7650
			2,3-Dichlorobutene-1		3:9074
$C_4H_2Cl_4$	M.W. = 191.9	Cl = 73.9%	3,4-Dichlorobutene-1		3:5350
1,2,3,4-Tetrachlorobutadiene-1,3					
Solid isomer		3:0870	1,1-Dichlorobutene-2		3:7685
Liquid isomer		3:6150	1,2-Dichlorobutene-2		
			Higher-boiling isomer		3:5615
$C_4H_2Cl_4$	M.W. = 262.8	Cl = 81.0%	Lower-boiling isomer		3:5360
1,1,2,3,4,4-Hexachlorobutene-2			1,3-Dichlorobutene-2		3:5550
Solid isomer		3:1945	1,4-Dichlorobutene-2		3:5725
Liquid isomer		3:9010			
Hexachlorobutene-X		3:9048			
Hexachlorobutene-Y		3:9050			

1-Chlorohexene-3	3:9336	2,3,4,6-Tetrachlorobenzal, (di)chloride	3:6980
3-Chlorohexene-3	3:7535	2,3,5,6-Tetrachlorobenzal (di)chloride	3:6980
3-Chloro-2-methylpentene-1	3:7660	$C_7H_5Cl_3$ M.W. = 264.4 Cl = 67.1%	
4-Chloro-4-methylpentene-1	3:7500	2,3,4,5,6-Pentachlorotoluene	3:4937
5-Chloro-2-methylpentene-2	3:7915		3:2312
4-Chloro-3-methylpentene-2	3:9333		3:2178
2-Chloro-3,3-dimethylbutene-1	3:7340		3:6910
1-Chloro-2,3-dimethylbutene-2	3:7520		3:0142
Chlorocyclohexane	3:8040	$C_7H_4Cl_4$ M.W. = 230.0 Cl = 61.7%	
$C_6H_{12}Cl_2$ M.W. = 155.1 Cl = 45.7%		2,3,4,5-Tetrachlorotoluene	3:2710
1,2-Dichlorohexane	3:8380	2,3,4,6-Tetrachlorotoluene	3:2480
1,5-Dichlorohexane	3:9340	2,3,5,6-Tetrachlorotoluene	3:2575
1,6-Dichlorohexane	3:6720	2,4-Dichlorobenzal (di)chloride	3:9399
2,2-Dichlorohexane	3:9342	2,5-Dichlorobenzal (di)chloride	3:0490
2,3-Dichlorohexane	3:8300	2,6-Dichlorobenzal (di)chloride	3:9393
2,5-Dichlorohexane	3:8525	3,4-Dichlorobenzal (di)chloride	3:6876
3,4-Dichlorohexane	3:9344	3,5-Dichlorobenzal (di)chloride	3:0370
2,3-Dichloro-2-methylpentane	3:9346	2-Chlorobenzotrichloride	3:6880
2,5-Dichloro-2-methylpentane	3:6540	3-Chlorobenzotrichloride	3:6845
3,3-Dichloro-2,2-dimethylbutane	3:4325	4-Chlorobenzotrichloride	3:6825
4,4-Dichloro-2,2-dimethylbutane	3:8132	$C_7H_5Cl_3$ M.W. = 195.5 Cl = 54.4%	
2,3-Dichloro-2,3-dimethylbutane	3:4520	2,3,4-Trichlorotoluene	3:0423
$C_6H_{10}Cl$ M.W. = 120.6 Cl = 29.4%		2,3,5-Trichlorotoluene	3:0610
1-Chlorohexane	3:7955	2,3,6-Trichlorotoluene	3:0623
2-Chlorohexane	3:7715	2,4,5-Trichlorotoluene	3:2100
3-Chlorohexane	3:7670	2,4,6-Trichlorotoluene	3:0380
1-Chloro-2-methylpentane	3:7563	3,4,5-Trichlorotoluene	3:0550
2-Chloro-2-methylpentane	3:7490	2,6-Dichlorobenzyl chloride	3:0410
3-Chloro-2-methylpentane	3:7565	3,4-Dichlorobenzyl chloride	3:6795
4-Chloro-2-methylpentane	3:7495	3,5-Dichlorobenzyl chloride	3:0350
5-Chloro-2-methylpentane	3:7695	2-Chlorobenzal (di)chloride	3:6625
1-Chloro-3-methylpentane	3:9348	3-Chlorobenzal (di)chloride	3:6710
2-Chloro-3-methylpentane	3:9350	4-Chlorobenzal (di)chloride	3:6700
3-Chloro-3-methylpentane	3:7585	Benzotrichloride	3:6540
3-(Chloromethyl)pentane	3:7720	$C_7H_4Cl_4$ M.W. = 161.0 Cl = 44.0%	
1-Chloro-2,2-dimethylbutane	3:7590	2,3-Dichlorotoluene	3:6345
3-Chloro-2,2-dimethylbutane	3:7475	2,4-Dichlorotoluene	3:6290
4-Chloro-2,2-dimethylbutane	3:7555	2,5-Dichlorotoluene	3:6245
2-Chloro-2,3-dimethylbutane	3:7600	2,6-Dichlorotoluene	3:6270
		3,4-Dichlorotoluene	3:6355
		3,5-Dichlorotoluene	3:6310
		2-Chlorobenzyl chloride	3:6400
		3-Chlorobenzyl chloride	3:6445
		4-Chlorobenzyl chloride	3:0220
		Benzal (di)chloride	3:6327
$C_7$ GROUP		$C_7H_5Cl$ M.W. = 126.6 Cl = 23.0%	
$C_7HCl_7$ M.W. = 333.3 Cl = 74.5%		2-Chlorotoluene	3:8245
Pentachlorobenzal (di)chloride	3:3590	3-Chlorotoluene	3:8275
$C_7H_2Cl_4$ M.W. = 298.8 Cl = 71.2%		4-Chlorotoluene	3:8287
2,3,4,5-Tetrachlorobenzal (di)chloride	3:9397		

1-Chloro-3-methylbutene-1	3: 7215	1,2-Dichlorobenzene	3: 6055
1-Chloro-2-methylbutene-2	3: 7485	1,3-Dichlorobenzene	3: 5960
3-Chloro-2-methylbutene-2	3: 7335	1,4-Dichlorobenzene	3: 0980
4-Chloro-2-methylbutene-2	3: 7465		
Chlorocyclopentane	3: 7545	$C_6H_5Cl$ M.W. = 112.6	Cl = 31.5%
		3-Chlorohexatetraene-1,3,4,5	3: 7735
$C_6H_5Cl_2$ M.W. = 175.5	Cl = 60.6%	Chlorobenzene	3: 7903
1,2,3-Trichloro-2-methylbutane	3: 6100	$C_6H_5Cl_2$ M.W. = 183.5	Cl = 58.0%
2,3,3-Trichloro-2-methylbutane	3: 4755	3,4,6-Trichlorohexatriene-1,2,4	3: 9302
4,4,4-Trichloro-2-methylbutane	3: 0216		
1,3-Dichloro-2-(chloro-methyl)butane	3: 9218	$C_6H_5Cl_2$ M.W. = 149.0	Cl = 47.6%
		3,6-Dichlorohexatriene-1,3,4	3: 9304
$C_6H_{10}Cl_2$ M.W. = 141.0	Cl = 50.3%	$C_6H_7Cl_4$ M.W. = 219.9	Cl = 64.5%
1,1-Dichloropentane	3: 8015	1,3,4,6-Tetrachlorohexadiene-2,4	3: 0306
1,2-Dichloropentane	3: 8140		
1,3-Dichloropentane	3: 9220	$C_6H_5Cl_6$ M.W. = 290.8	Cl = 73.1%
1,4-Dichloropentane	3: 9224	1,2,3,4,5,6-Hexachlorohexene-3	3: 1220
1,5-Dichloropentane	3: 8575	1,2,3,4,5,6-Hexachlorocyclohexane	
2,2-Dichloropentane	3: 7755	Higher-melting isomer ( <i>trans</i> )	3: 4990
2,3-Dichloropentane	3: 8010	Lower-melting isomer ( <i>cis</i> )	3: 4410
2,4-Dichloropentane	3: 8120		
3,3-Dichloropentane	3: 7895	$C_6H_7Cl_3$ M.W. = 185.5	Cl = 57.4%
1,2-Dichloro-2-methylbutane	3: 7920	3,3,6-Trichlorohexadiene-1,4	3: 0308
1,3-Dichloro-2-methylbutane	3: 9223		
1,4-Dichloro-2-methylbutane	3: 8360	$C_6H_5Cl_2$ M.W. = 151.0	Cl = 47.0%
2,3-Dichloro-2-methylbutane	3: 7975	1,3-Dichlorohexadiene-2,4	3: 9310
2,4-Dichloro-2-methylbutane	3: 8105		
3,3-Dichloro-2-methylbutane	3: 9230	$C_6H_5Cl$ M.W. = 116.6	Cl = 30.4%
3,4-Dichloro-2-methylbutane	3: 8075	3-Chlorohexadiene-1,8	3: 9312
4,4-Dichloro-2-methylbutane	3: 7885		
$C_6H_{11}Cl$ M.W. = 106.6	Cl = 33.3%	1-Chloro-3-methylpentadiene-1,2	3: 9314
1-Chloropentane	3: 7460	1-Chloro-3-methylpentadiene-1,3	3: 9316
2-Chloropentane	3: 7325	2-Chloro-3-methylpentadiene-1,3	3: 9318
3-Chloropentane	3: 7330		
1-Chloro-2-methylbutane	3: 7345	1-Chlorohexyne-1	3: 9320
2-Chloro-2-methylbutane	3: 7220	3-Chloro-3-methylpentyne-1	3: 9322
3-Chloro-2-methylbutane	3: 7275	4-Chloro-4-methylpentyne-2	3: 9324
4-Chloro-2-methylbutane	3: 7365		
1-Chloro-2,2-dimethylpropane	3: 7200	$C_6H_5Cl_2$ M.W. = 187.5	Cl = 56.7%
$C_6$ GROUP		1,1,2-Trichlorohexene-1	3: 0326
$C_6HCl_4$ M.W. = 250.4	Cl = 70.8%		
Pentachlorobenzene	3: 2290	$C_6H_5Cl_3$ M.W. = 258.4	Cl = 68.6%
		1,1,1,2,2-Pentachlorohexane	3: 9328
$C_6H_2Cl_4$ M.W. = 215.0	Cl = 65.7%	$C_6H_{10}Cl_2$ M.W. = 153.1	Cl = 46.3%
1,2,3,4-Tetrachlorobenzene	3: 0655	1,2-Dichlorohexene-1	3: 0330
1,2,3,5-Tetrachlorobenzene	3: 0915		
1,2,4,5-Tetrachlorobenzene	3: 4115	$C_6H_{10}Cl_4$ M.W. = 224.0	Cl = 63.3%
		1,1,2,2-Tetrachlorohexane	3: 9332
$C_6H_2Cl_4$ M.W. = 161.5	Cl = 58.6%	$C_6H_{11}Cl$ M.W. = 118.6	Cl = 29.9%
1,2,3-Trichlorobenzene	3: 0290	1-Chlorohexene-1	3: 7630
1,2,4-Trichlorobenzene	3: 6420	2-Chlorohexene-1	3: 7530
1,3,5-Trichlorobenzene	3: 1400	3-Chlorohexene-1	3: 8334
		4-Chlorohexene-1	3: 7655
		5-Chlorohexene-1	3: 7665
$C_6H_4Cl_2$ M.W. = 147.0	Cl = 45.2%	1-Chlorohexene-2	3: 7620
3,4-Dichlorohexatetraene-1,2,4,5	3: 9300	4-Chlorohexene-2	3: 7675

$C_8H_{15}Cl$	M.W. = 146.7	Cl = 24.2%	2-Chloro-3,4-dimethylhexane	3:9558
2-Chloro-octene-1		3:8346	4-(Chloromethyl)-3-methylhexane	3:9500
3-Chloro-octene-1		3:9518		
2-Chloro-octene-2		3:8345	3-Chloro-3-ethyl-2-methylpentane	3:8210
4-Chloro-octene-2		3:8185	4-Chloro-2,2,4-trimethylpentane	3:8113
4-Chloro-octene-4		3:8230	1-Chloro-2,2,3,3-tetramethylbutane	3:0945
4-Chloro-6-methylheptene-1		3:8205		
6-Chloro-2-methylheptene-2		3:9520	<b>C<sub>9</sub> GROUP</b>	
4-Chloro-3-methylheptene-2		3:9524	$C_9H_{19}Cl$	M.W. = 152.6
4-Chloro-6-methylheptene-2		3:9525	1-Chloro-1-phenylpropene-1	Cl = 23.2%
5-Chloro-4-methylheptene-3		3:9526	2-Chloro-1-phenylpropene-1	3:0604
4-Chloro-2,5-dimethylhexene-2		3:9529	3-Chloro-1-phenylpropene-1	3:9606
4-Chloro-3,5-dimethylhexene-2		3:9528	1-Chloro-2-phenylpropene-1	3:8742
2-Chloro-2,5-dimethylhexene-3		3:9527	1-Chloro-3-phenylpropene-1	3:8737
1-Chloro-4-ethylhexene-3		3:8510	2-Chloro-3-phenylpropene-1	3:9608
2-Chloro-3-ethyl-3-methylpentene-1		3:8115	$C_9H_{11}Cl$	M.W. = 154.6
			$\gamma$ -Phenyl- <i>n</i> -propyl chloride	Cl = 22.9%
			4-Chloro-isopropylbenzene	3:8705
			$\alpha$ -Chloro-isopropylbenzene	3:9610
			2-Chloro-1,3,5-trimethylbenzene	3:8725
$C_8H_{15}Cl_2$	M.W. = 183.1	Cl = 38.7%	$C_9H_{15}Cl$	M.W. = 158.7
1,6-Dichloro-octane		3:9530	2-Chloro-6-methyl-5-methylenheptene-2	Cl = 22.4%
1,7-Dichloro-octane		3:9532		
1,8-Dichloro-octane		3:8805	1-Chlorononyne-1	3:9618
2,2-Dichloro-octane		3:8670	2-Chloro-2-methyloctyne-3	3:9622
4-Chloro-3-(chloromethyl)heptane		3:9534	$C_9H_{17}Cl$	M.W. = 160.7
2,5-Dichloro-2,5-dimethylhexane		3:1550	4-Chloro-7-methyloctene-2	Cl = 22.1%
3,4-Dichloro-3,4-dimethylhexane		3:8315		
3,3-Dichloro-2,2,4-trimethylpentane		3:9536	5-Chloro-4-methyloctene-3	3:9624
			4-Chloro-3,6-dimethylheptene-2	3:9630
$C_8H_{17}Cl$	M.W. = 148.7	Cl = 23.9%	$C_9H_{15}Cl_2$	M.W. = 197.1
1-Chloro-octane		3:8585	1,2-Dichlorononane	Cl = 36.0%
2-Chloro-octane		3:8378	1,9-Dichlorononane	3:8880
4-Chloro-octane		3:9533	2,6-Dichloro-2,6-dimethylheptane	3:0455
2-Chloro-2-methylheptane		3:8100	$C_9H_{15}Cl$	M.W. = 162.7
6-Chloro-2-methylheptane		3:9540	1-Chlorononane	Cl = 21.8%
3-Chloro-3-methylheptane		3:9544	2-Chlorononane	3:8635
3-(Chloromethyl)heptane		3:8370	3-Chlorononane	3:9638
3-Chloro-4-methylheptane		3:9548	5-Chlorononane	3:9640
4-Chloro-4-methylheptane		3:9550	3-Chloro-3-methyloctane	3:0642
1-Chloro-3-ethylhexane		3:9552	4-Chloro-4-methyloctane	3:9644
3-Chloro-3-ethylhexane		3:8223	3-Chloro-3-ethylheptane	3:9640
3-Chloro-2,3-dimethylhexane		3:9554	4-Chloro-4-ethylheptane	3:0648
2-Chloro-2,5-dimethylhexane		3:9556		

Benzyl chloride	3:8535	4-Chloro-2,2-dimethylpentane	3:9440
$C_7H_5Cl$ M.W. = 128.6 Cl = 27.6%		2-Chloro-2,3-dimethylpentane	3:9442
5-Chloro-5-methylhexen-1-yne-3	3:9103	3-Chloro-2,3-dimethylpentane	3:7970
$C_7H_{11}Cl$ M.W. = 130.6 Cl = 27.1%		5-Chloro-2,3-dimethylpentane	3:8153
4-Chloroheptadiene-1,6	3:8085	2-Chloro-2,4-dimethylpentane	3:7750
1-Chloro-3-ethylpentadiene-1,2	3:9406	3-Chloro-2,2,3-trimethylbutane	3:4020
1-Chloroheptyne-1	3:8032	<b>C<sub>8</sub> GROUP</b>	
1-Chloro-3-ethylpentyne-1	3:9410	$C_8H_7Cl$ M.W. = 136.6 Cl = 25.1%	
$C_7H_{13}Cl$ M.W. = 132.6 Cl = 26.7%		$\omega$ -Chlorophenylacetylene	3:9494
1-Chloroheptene-1	3:8219	<i>o</i> -Chlorophenylacetylene	3:9497
2-Chloroheptene-1	3:7988	<i>m</i> -Chlorophenylacetylene	3:9500
3-Chloroheptene-1	3:9412	<i>p</i> -Chlorophenylacetylene	3:0590
4-Chloroheptene-2	3:8050	$C_8H_7Cl$ M.W. = 138.6 Cl = 25.6%	
4-Chloroheptene-3	3:8023	$\alpha$ -Chlorovinylbenzene	3:8715
4-Chloro-5-methylhexene-1	3:7730	$\beta$ -Chlorobutylbenzene	3:8717
4-Chloro-3-methylhexene-2	3:9414	$C_8H_8Cl_2$ M.W. = 175.1 Cl = 40.5%	
4-Chloro-5-methylhexene-2	3:7890	Styrene dichloride	3:6685
4-Chloro-2,4-dimethylpentene-1	3:7725	<i>o</i> -Xylylene (di)chloride	3:1040
3-Chloro-2,4-dimethylpentene-2	3:7605	<i>m</i> -Xylylene (di)chloride	3:0310
4-Chloro-2,4-dimethylpentene-2	3:0418	<i>p</i> -Xylylene (di)chloride	3:2825
$C_7H_{14}Cl_2$ M.W. = 169.1 Cl = 41.9%		$C_8H_9Cl$ M.W. = 140.6 Cl = 25.2%	
1,1-Dichloroheptane	3:8650	3-Chloro-1,2-dimethylbenzene	3:8645
1,2-Dichloroheptane	3:9420	4-Chloro-1,2-dimethylbenzene	3:8675
1,7-Dichloroheptane	3:9422	2-Chloro-1,3-dimethylbenzene	3:8590
2,2-Dichloroheptane	3:9424	4-Chloro-1,3-dimethylbenzene	3:8665
4,4-Dichloroheptane	3:9426	5-Chloro-1,3-dimethylbenzene	3:8640
4,5-Dichloro-2,2-dimethylpentane	3:8516	2-Chloro-1,4-dimethylbenzene	3:8600
2,4-Dichloro-2,4-dimethylpentane	3:9423	2-Chloroethylbenzene	3:8550
3,3-Dichloro-2,4-dimethylpentane	3:7610	4-Chloroethylbenzene	3:8570
1,5-Dichloro-3,3-dimethylpentane	3:9430	2-Methylbenzyl ( <i>o</i> -xylyl) chloride	3:8710
$C_7H_{15}Cl$ M.W. = 134.7 Cl = 26.3%		3-Methylbenzyl ( <i>m</i> -xylyl) chloride	3:8700
1-Chloroheptane	3:8250	4-Methylbenzyl ( <i>p</i> -xylyl) chloride	3:8660
2-Chloroheptane	3:9432	$\alpha$ -Chloroethylbenzene	3:8667
3-Chloroheptane	3:8080	$\beta$ -Chloroethylbenzene	3:8712
4-Chloroheptane	3:8095	$C_8H_{12}Cl_2$ M.W. = 179.1 Cl = 39.6%	
2-Chloro-2-methylhexane	3:7945	2,5-Dichloro-2,5-dimethylhexyne-3	3:9504
5-Chloro-2-methylhexane	3:7935	$C_8H_{13}Cl$ M.W. = 144.6 Cl = 24.5%	
1-Chloro-3-methylhexane	3:8155	3-Chloro-octadiene-1,3	3:9506
2-Chloro-3-methylhexane	3:9434	1-Chloro-octyne-1	3:0510
3-Chloro-3-methylhexane	3:7950	1-Chloro-octyne-2	3:9514
4-Chloro-3-methylhexane	3:9436	3-Chloro-3-methylheptyne-4	3:9516
2-Chloro-3-ethylpentane	3:9438		
3-Chloro-3-ethylpentane	3:8055		



$C_8H_{15}Cl$  M.W. = 146.7 Cl =

2-Chloro-octene-1

3-Chloro-octene-1

2-Chloro-octene-2

4-Chloro-octene-2

4-Chloro-octene-4

4-Chloro-6-methylheptene-1

6-Chloro-2-methylheptene-2

4-Chloro-3-methylheptene-2

4-Chloro-6-methylheptene-2

5-Chloro-4-methylheptene-3

4-Chloro-2,5-dimethylhexene-2

4-Chloro-3,5-dimethylhexene-2

2-Chloro-2,5-dimethylhexene-3

1-Chloro-4-ethylhexene-3

2-Chloro-3-ethyl-3-methyl-  
pentene-1

$C_8H_{17}Cl_2$  M.W. = 183.1 Cl =

1,6-Dichloro-octane

1,7-Dichloro-octane

1,8-Dichloro-octane

2,2-Dichloro-octane

4-Chloro-3-(chloromethyl)heptane

2,5-Dichloro-2,5-dimethylhexane

3,4-Dichloro-3,4-dimethylhexane

3,3-Dichloro-2,2,4-trimethylpentane

$C_8H_{17}Cl$  M.W. = 148.7 Cl =

1-Chloro-octane

2-Chloro-octane

4-Chloro-octane

2-Chloro-2-methylheptane

6-Chloro-2-methylheptane

3-Chloro-3-methylheptane

3-(Chloromethyl)heptane

3-Chloro-4-methylheptane

4-Chloro-4-methylheptane

1-Chloro-3-ethylhexane

3-Chloro-3-ethylhexane

3-Chloro-2,3-dimethylhexane

2-Chloro-2,5-dimethylhexane



$C_{12}H_{26}Cl$ 1-Chlorododecane	M.W. = 204.8 Cl = 17.3% 3:8810	1,1,2,2-Tetrachloro-1,2-diphenylethane 1,1-Dichloro-2-( <i>o</i> -chlorophenyl)-ethane 1,1-Dichloro-2,2- <i>bis</i> -( <i>p</i> -chlorophenyl)ethane	3:4496 3:1890 3:3320
<b>C<sub>13</sub> GROUP</b>			
$C_{13}H_{10}Cl_2$ Benzophenone dichloride 4,4'-Dichlorodiphenylmethane	M.W. = 237.1 Cl = 29.9% 3:6960 3:1057	$C_{14}H_{11}Cl_2$ 1,1,1-Trichloro-2,2-diphenylethane $C_{14}H_{13}Cl_2$ 1,1-Di-( <i>p</i> -chlorophenyl)ethane 1,1-Dichloro-2,2-diphenylethane	Cl = 37.2% 3:1420 Cl = 28.3% 3:0995 3:1940
$C_{13}H_{11}Cl$ Benzohydril chloride	M.W. = 202.7 Cl = 17.5% 3:0060		
$C_{13}H_{21}Cl$ 1-Chlorotridecane	M.W. = 218.8 Cl = 16.2% 3:9559		
<b>C<sub>14</sub> GROUP</b>			
$C_{14}H_8Cl_2$ 9,10-Dichloroanthracene	M.W. = 247.1 Cl = 23.7% 3:4916	<i>d,l</i> -1,2-Dichloro-1,2-diphenylethane <i>meso</i> -1,2-Dichloro-1,2-diphenylethane	3:2570 3:4854
$C_{14}H_8Cl_4$ 1,1-Dichloro-2-( <i>o</i> -chlorophenyl)-2-( <i>p</i> -chlorophenyl)ethylene	M.W. = 318.0 Cl = 44.6% 3:19250	$C_{14}H_{11}Cl$ 1,1-Diphenylethyl chloride 2,2-Diphenylethyl chloride	Cl = 11.7% 3:9370 3:9371
1,1-Dichloro-2-( <i>m</i> -chlorophenyl)-2-( <i>p</i> -chlorophenyl)ethylene	3:9963	$C_{14}H_{19}Cl$ 1-Chlorotetradecane	M.W. = 232.8 Cl = 15.2% 3:9374
1,1-Dichloro-2,2- <i>bis</i> -( <i>p</i> -chlorophenyl)ethylene	3:2438	<b>C<sub>15</sub> GROUP</b>	
$C_{14}H_8Cl_4$ 1,1,1,2-Tetrachloro-2,2- <i>bis</i> -( <i>p</i> -chlorophenyl)ethane	M.W. = 388.9 Cl = 54.7% 3:2477	$C_{15}H_{11}Cl$ 1-Chloropentadecane	M.W. = 246.9 Cl = 14.4% 3:9390
$C_{14}H_9Cl_2$ 1-Chloro-2,2- <i>bis</i> -( <i>p</i> -chlorophenyl)-ethylene	M.W. = 283.6 Cl = 37.5% 3:1430	<b>C<sub>16</sub> GROUP</b>	
$C_{14}H_9Cl_4$ "o,o'-DDT" "o,p'-DDT" "m,p'-DDT" "p,p'-DDT" (ordinary DDT)	M.W. = 354.5 Cl = 50.0% 3:9865 3:1820 3:9867 3:3298	$C_{16}H_{13}Cl$ 1-Chlorohexadecane	M.W. = 260.9 Cl = 13.6% 3:0015
$C_{14}H_{10}Cl_2$ 1,1-Dichloro-2,2-diphenylethylene 1,1-Di-( <i>p</i> -chlorophenyl)ethylene	M.W. = 249.1 Cl = 28.5% 3:1938 3:2475	<b>C<sub>17</sub> GROUP</b>	
<i>cis</i> -1,2-Dichloro-1,2-diphenylethylene <i>trans</i> -1,2-Dichloro-1,2-diphenylethylene	3:1380 3:4210	$C_{17}H_{15}Cl$ 1-Chloroheptadecane	M.W. = 274.0 Cl = 12.0% 3:0100
$C_{14}H_{10}Cl_4$	M.W. = 320.1 Cl = 44.3%	<b>C<sub>18</sub> GROUP</b>	
		$C_{18}H_{17}Cl$ 1-Chlorooctadecane	M.W. = 288.9 Cl = 12.3% 3:0095
		<b>C<sub>19</sub> GROUP</b>	
		$C_{19}H_{19}Cl$ Triphenylchloromethane	M.W. = 278.8 Cl = 12.7% 3:3410
		<b>C<sub>20</sub> GROUP</b>	
		$C_{20}H_{15}Cl$ 1-Chloro-1,2,2-triphenylethylene	M.W. = 290.8 Cl = 12.2% 3:3560

#### D. COMPOUNDS CONTAINING ONLY CARBON, HYDROGEN, OXYGEN, AND CHLORINE

<b>C<sub>2</sub> GROUP</b>			
$C_2HOCl_2$ Trichloroacetaldehyde (chloral)	M.W. = 147.4 Cl = 72.2% 3:5210	Dichloromethyl chloroformate	3:5315
Dichloroacetyl chloride	3:5290	$C_2H_3OCl_2$ Dichloroacetaldehyde	M.W. = 112.9 Cl = 62.8% 3:6180
$C_2HO_2Cl_2$ Trichloroacetic acid	M.W. = 163.4 Cl = 65.1% 3:1150	Chloroacetyl chloride	3:5235
		$C_2H_3O_2Cl_2$ Dichloroacetic acid	M.W. = 128.9 Cl = 55.0% 3:6208

Chloromethyl chloroformate	3:5275	$C_3H_5OCl_2$ M.W. = 161.4	Cl = 65.9%
$C_2H_5OCl$ M.W. = 78.5	Cl = 45.2%	$\alpha, \alpha, \beta$ -Trichloropropionaldehyde	3:9033
Chloroacetaldehyde	3:7212	$\alpha, \alpha, \alpha$ -Trichloroacetone	3:5620
Acetyl chloride	3:7065	$\alpha, \alpha, \gamma$ -Trichloroacetone	3:5957
$C_2H_5OCl_2$ M.W. = 149.4	$\bar{Cl}$ = 71.2%	$\alpha, \alpha$ -Dichloropropionyl chloride	3:5372
2,2,2-Trichloroethanol-1	3:5775	$\alpha, \beta$ -Dichloropropionyl chloride	3:9032
$C_2H_5O_2Cl$ M.W. = 94.5	Cl = 37.5%	$\beta, \beta$ -Dichloropropionyl chloride	3:9032-A
Chloroacetic acid	3:1370	3,3,3-Trichloro-1,2-epoxypropane	3:5760
Methyl chloroformate	3:5075	$C_3H_5O_2Cl$ M.W. = 106.5	Cl = 33.3%
$C_2H_5O_2Cl_2$ M.W. = 165.4	Cl = 64.3%	$\alpha$ -Chloroacrylic acid	3:1445
Choral hydrate	3:1270	$\beta$ -Chloroacrylic acid	3:2240
$C_2H_4OCl_2$ M.W. = 115.0	Cl = 61.7%	$C_3H_5O_2Cl_2$ M.W. = 177.4	Cl = 56.0%
2,2-Dichloroethanol-1	3:5745	$\alpha, \alpha, \beta$ -Trichloropropionic acid	3:1275
<i>sym.</i> -Dichlorodimethyl ether	3:5245	Methyl trichloroacetate	3:5800
$C_2H_5O_2Cl_2$ M.W. = 131.0	Cl = 54.2%	$C_3H_5OCl_2$ M.W. = 127.0	Cl = 55.9%
Dichloroacetaldehyde hydrate	3:1055	$\alpha, \alpha$ -Dichloropropionaldehyde	3:9033-A
$C_2H_4OCl$ M.W. = 80.5	Cl = 44.0%	$\alpha, \beta$ -Dichloropropionaldehyde	3:9034
Ethylene chlorhydrin	3:5552	<i>sym.</i> -Dichloroacetone	3:0563
Chloromethyl methyl ether	3:7085	<i>unsym.</i> -Dichloroacetone	3:5430
Ethyl hypochlorite	3:7022	$\alpha$ -Chloropropionyl chloride	3:5320
<b>C<sub>3</sub> GROUP</b>		$\beta$ -Chloropropionyl chloride	3:5090
$C_3HOC_2Cl_4$ M.W. = 230.3	Cl = 77.0%	$C_3H_4OCl_4$ M.W. = 197.9	Cl = 71.7%
Pentachloroacetone	3:6205	1,1,1,3-Tetrachloropropanol-2	3:9030
$C_3H_2O_2Cl$ M.W. = 104.5	Cl = 33.9%	1,1,3,3-Tetrachloropropanol-2	3:9037
Chloropropionic acid	3:1685	$C_3H_4O_2Cl_2$ M.W. = 143.0	Cl = 49.6%
$C_3H_2O_2Cl_2$ M.W. = 175.4	Cl = 60.6%	$\alpha, \alpha$ -Dichloropropionic acid	3:6162
$\alpha, \beta$ -Trichloroacrylic acid	3:1840	$\alpha, \beta$ -Dichloropropionic acid	3:0555
$C_3H_2O_2Cl_4$ M.W. = 246.3	Cl = 72.0%	$\beta, \beta$ -Dichloropropionic acid	3:1038
Pentachloropropionic acid	3:4395	Methyl dichloroacetate	3:5655
$C_3H_2OCl_4$ M.W. = 105.9	Cl = 72.4%	$\beta$ -Chloroethyl chloroformate	3:5780
<i>sym.</i> -Tetrachloroacetone	3:6050	$C_3H_4OCl$ M.W. = 92.5	Cl = 38.3%
<i>unsym.</i> -Tetrachloroacetone	3:6045	$\beta$ -Chloroallyl alcohol	3:5635
$C_3H_4O_2Cl_2$ M.W. = 141.0	Cl = 50.3%	$\gamma$ -Chloroallyl alcohol	3:5820
$\alpha, \beta$ -Dichloroacrylic acid	3:2265	$\alpha$ -Chloropropionaldehyde	3:5160
$\beta, \beta$ -Dichloroacrylic acid	3:1875	$\beta$ -Chloropropionaldehyde	3:5576
Malonyl (di)chloride	3:9030	Chloroacetone	3:5425
$C_4H_5O_2Cl_4$ M.W. = 211.9	Cl = 66.9%	Propionyl chloride	3:7170
$\alpha, \alpha, \beta, \beta$ -Tetrachloropropionic acid	3:1450	3-Chloro-1,2-epoxypropane (Epichlorohydrin)	3:5358
$C_3H_5OCl$ M.W. = 90.5	Cl = 39.2%	$C_3H_5OCl_2$ M.W. = 163.4	Cl = 64.5%
$\alpha$ -Chloroacrolein	3:9031	1,1,1-Trichloropropanol-2	3:0946
Acryloyl chloride	3:7153	$C_3H_4O_2Cl$ M.W. = 108.5	Cl = 32.7%
		$\alpha$ -Chloropropionic acid	3:0123
		$\beta$ -Chloropropionic acid	3:0160

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Chloromethyl chloroformate	3:5275	$C_2H_3OCl_3$ M.W. = 161.4	Cl = 65.9%
$C_2H_3OCl$ M.W. = 78.5	Cl = 45.2%	$\alpha, \alpha, \beta$ -Trichloropropionaldehyde	3:9033
Chloroacetaldehyde	3:7212	$\alpha, \alpha, \alpha$ -Trichloroacetone	3:5620
Acetyl chloride	3:7065	$\alpha, \alpha, \gamma$ -Trichloroacetone	3:5957
$C_2H_3OCl_2$ M.W. = 149.4	Cl = 71.2%	$\alpha, \alpha$ -Dichloropropionyl chloride	3:5372
2,2,2-Trichloroethanol-1	3:5775	$\alpha, \beta$ -Dichloropropionyl chloride	3:9032
$C_2H_3O_2Cl$ M.W. = 94.5	Cl = 37.5%	$\beta, \beta$ -Dichloropropionyl chloride	3:0032-A
Chloroacetic acid	3:1370	3,3,3-Trichloro-1,2-epoxypropano	3:5760
Methyl chloroformate	3:5075	$C_2H_3O_2Cl$ M.W. = 106.5	Cl = 33.3%
$C_2H_3O_2Cl_2$ M.W. = 165.4	Cl = 64.3%	$\alpha$ -Chloroacrylic acid	3:1445
Choral hydrate	3:1270	$\beta$ -Chloroacrylic acid	3:2240
$C_2H_4OCl_2$ M.W. = 115.0	Cl = 61.7%	$C_2H_3O_2Cl_2$ M.W. = 177.4	Cl = 56.0%
2,2-Dichloroethanol-1	3:5745	$\alpha, \alpha, \beta$ -Trichloropropionic acid	3:1275
<i>sym.</i> -Dichlorodimethyl ether	3:5245	Methyl trichloroacetate	3:5800
$C_2H_4O_2Cl_2$ M.W. = 131.0	Cl = 54.2%	$C_2H_3OCl_2$ M.W. = 127.0	Cl = 55.9%
Dichloroacetaldehyde hydrate	3:1035	$\alpha, \alpha$ -Dichloropropionaldehyde	3:9033-A
$C_2H_3OCl$ M.W. = 80.5	Cl = 44.0%	$\alpha, \beta$ -Dichloropropionaldehyde	3:0034
Ethylene chlorohydrin	3:5552	<i>sym.</i> -Dichloroacetone	3:0563
Chloromethyl methyl ether	3:7035	<i>unsym.</i> -Dichloroacetone	3:5430
Ethyl hypochlorite	3:7022	$\alpha$ -Chloropropionyl chloride	3:5320
<b>C<sub>3</sub> GROUP</b>		$\beta$ -Chloropropionyl chloride	3:5690
$C_3HOCl_4$ M.W. = 230.3	Cl = 77.0%	$C_3H_4OCl_4$ M.W. = 197.0	Cl = 71.7%
Pentachloroacetone	3:6203	1,1,1,3-Tetrachloropropanol-2	3:0036
$C_3HO_2Cl$ M.W. = 104.5	Cl = 33.9%	1,1,3,3-Tetrachloropropanol-2	3:0037
Chloropropionic acid	3:1693	$C_3H_4O_2Cl_2$ M.W. = 143.0	Cl = 49.6%
$C_3HO_2Cl_2$ M.W. = 175.4	Cl = 60.6%	$\alpha, \alpha$ -Dichloropropionic acid	3:6162
$\alpha, \beta, \beta$ -Trichloroacrylic acid	3:1840	$\alpha, \beta$ -Dichloropropionic acid	3:0355
$C_3HO_2Cl_3$ M.W. = 246.3	Cl = 72.0%	$\beta, \beta$ -Dichloropropionic acid	3:1058
Pentachloropropionic acid	3:4595	Methyl dichloroacetate	3:5655
$C_3H_3OCl_4$ M.W. = 195.0	Cl = 72.4%	$\beta$ -Chloroethyl chloroformate	3:5780
<i>sym.</i> -Tetrachloroacetone	3:6030	$C_3H_3OCl$ M.W. = 92.5	Cl = 38.3%
<i>unsym.</i> -Tetrachloroacetone	3:6035	$\beta$ -Chloroallyl alcohol	3:5635
$C_3H_3O_2Cl_2$ M.W. = 141.0	Cl = 50.3%	$\gamma$ -Chloroallyl alcohol	3:5820
$\alpha, \beta$ -Dichloroacrylic acid	3:2265	$\alpha$ -Chloropropionaldehyde	3:5160
$\beta, \beta$ -Dichloroacrylic acid	3:1875	$\beta$ -Chloropropionaldehyde	3:5376
Malonyl (di)chloride	3:9030	Chloroacetone	3:5425
$C_3H_3O_2Cl_3$ M.W. = 211.0	Cl = 64.9%	Propionyl chloride	3:7170
$\alpha, \alpha, \beta, \beta$ -Tetrachloropropionic acid	3:1850	3-Chloro-1,2-epoxypropane (Epichlorohydrin)	3:5358
$C_3H_3OCl$ M.W. = 90.5	Cl = 33.2%	$C_3H_3OCl_2$ M.W. = 163.4	Cl = 64.5%
$\alpha$ -Chloroacrolein	3:9031	1,1,1-Trichloropropanol-2	3:0346
Acetyl chloride	3:7153	$C_3H_3O_2Cl$ M.W. = 108.5	Cl = 32.7%
		$\alpha$ -Chloropropionic acid	3:6125
		$\beta$ -Chloropropionic acid	3:0160

Methoxyacetyl chloride	3:5225	$C_4H_7O_3Cl_2$	M.W. = 171.0	Cl = 41.5%
Chloromethyl acetate	3:5356	Diglycoloyl dichloride		3:9092
Methyl chloroacetate	3:5585	Chloroacetic acid anhydride		3:0730
Ethyl chloroformate	3:7295	$C_4H_7O_4Cl_2$	M.W. = 187.0	Cl = 37.9%
$C_2H_6OCl_2$	M.W. = 129.0	<i>d,l</i> , $\alpha,\alpha'$ -Dichlorosuccinic acid		3:4711
2,3-Dichloropropanol-1	3:6060	<i>meso</i> , $\alpha,\alpha'$ -Dichlorosuccinic acid		3:4930
1,1-Dichloropropanol-2	3:5755	$C_4H_7OCl$	M.W. = 104.5	Cl = 33.9%
1,3-Dichloropropanol-2	3:5935	$\alpha$ -Chlorocrotonaldehyde		3:8117
$C_2H_7OCl$	M.W. = 94.5	$\alpha$ -Crotonoyl chloride		3:7693
2-Chloropropanol-1	3:7917	$C_4H_7OCl_3$	M.W. = 175.5	Cl = 60.6%
3-Chloropropanol-1	3:8285	$\alpha,\alpha,\beta$ -Trichloro- <i>n</i> -butyraldehyde		3:5910
1-Chloropropanol-2	3:7747	$\alpha,\alpha,\gamma$ -Trichloro- <i>n</i> -butyraldehyde		3:9094
Chloromethyl ethyl ether	3:7195	$C_4H_7O_2Cl$	M.W. = 120.5	Cl = 29.4%
$\alpha$ -Chloroethyl methyl ether	3:7150	$\alpha$ -Chlorocrotonic acid		3:2760
$\beta$ -Chloroethyl methyl ether	3:7265	$\alpha$ -Chloroisocrotonic acid		3:1615
$C_2H_7O_2Cl$	M.W. = 110.5	$\beta$ -Chlorocrotonic acid		3:2625
3-Chloropropanediol-1,2	3:9038	$\beta$ -Chloroisocrotonic acid		3:1300
2-Chloropropanediol-1,3	3:9039	$\gamma$ -Chlorocrotonic acid		3:2170
<b>C<sub>4</sub> GROUP</b>		Acetoacetyl chloride		3:9005
$C_4H_7O_2Cl_3$	M.W. = 187.4	Methyl $\alpha$ -chloroacrylate		3:9096
Chlorofumaryl (di)chloride	3:6105	Allyl chloroformate		3:7487
Chloromaleyl (di)chloride	3:6158	Isopropenyl chloroformate		3:7358
$C_4H_7O_2Cl$	M.W. = 132.5	$C_4H_7O_2Cl_3$	M.W. = 191.5	Cl = 55.6%
Chloromaleic acid anhydride	3:0280	$\alpha,\alpha,\beta$ -Trichloro- <i>n</i> -butyric acid		3:1280
$C_4H_7O_2Cl_3$	M.W. = 349.8	$\alpha,\alpha,\gamma$ -Trichloro- <i>n</i> -butyric acid		3:1831
$\alpha,\alpha',\beta,\beta,\beta',\beta',\beta'$ -Octachlorodiethyl ether	3:0738	$\alpha,\beta,\beta$ -Trichloro- <i>n</i> -butyric acid		3:0925
$C_4H_7O_2Cl_2$	M.W. = 153.0	$\gamma,\gamma,\gamma$ -Trichloro- <i>n</i> -butyric acid		3:1000
Fumaryl (di)chloride	3:5876	Ethyl trichloroacetate		3:5950
$C_4H_7O_2Cl_4$	M.W. = 223.9	$C_4H_7O_3Cl$	M.W. = 136.5	Cl = 26.0%
<i>d,l</i> , $\alpha,\alpha'$ -Dichlorosuccinyl (di)chloride	3:0395	Ethoxalyl chloride		3:5625
<i>meso</i> , $\alpha,\alpha'$ -Dichlorosuccinyl (di)chloride	3:9087	Carbomethoxyacetyl chloride		3:9098-A
$C_4H_7O_2Cl_4$	M.W. = 239.9	$C_4H_7O_3Cl_3$	M.W. = 207.5	Cl = 51.3%
Dichloroacetic acid anhydride	3:6430	$\beta$ -Hydroxyethyl trichloroacetate		3:9099
$C_4H_7O_4Cl_2$	M.W. = 185.0	$C_4H_7OCl_2$	M.W. = 141.0	Cl = 50.3%
Dichloromaleic acid	3:3634	$\alpha$ -Chloro- <i>n</i> -butyryl chloride		3:5570
$C_4H_7O_4Cl$	M.W. = 150.5	$\beta$ -Chloro- <i>n</i> -butyryl chloride		3:9100
Chlorofumaric acid	3:4853	$\gamma$ -Chloro- <i>n</i> -butyryl chloride		3:5970
Chloromaleic acid	3:3432	$\alpha$ -Chloroisobutyryl chloride		3:5385
$C_4H_7O_2Cl_2$	M.W. = 155.0	$\beta$ -Chloroisobutyryl chloride		3:9101
Succinyl (di)chloride	3:6200	$\alpha,\beta$ -Dichloro- <i>n</i> -butyraldehyde		3:9102
$\gamma$ -Chloroacetoacetyl chloride	3:9088	1,3-Dichlorobutanone-2		3:5900
$C_4H_7O_2Cl_4$	M.W. = 225.9	$\alpha,\beta$ -Dichlorovinyl ethyl ether		3:5540
$\beta$ -Chloroethyl trichloroacetate	3:6510	$C_4H_7O_2Cl_2$	M.W. = 157.0	Cl = 45.2%
		$\alpha,\beta$ -Dichloro- <i>n</i> -butyric acid		
		High-melting isomer		3:1003
		Low-melting isomer		3:1375

2,3-Dichlorodioxane-1,4	3:0105	Methyl $\alpha$ -chloropropionate	3:7908
$\beta$ -Chloroethyl chloroacetate	3:6230	Methyl $\beta$ -chloropropionate	3:5765
Ethyl dichloroacetate	3:5830	<i>n</i> -Propyl chloroformate	3:7540
Methyl $\alpha,\beta$ -dichloropropionate	3:9103	Isopropyl chloroformate	3:7405
$\gamma$ -Chloro- <i>n</i> -propyl chloroformate	3:6010	$C_4H_7O_2Cl_2$ M.W. = 193.5	Cl = 55.0%
$C_4H_7O_2Cl_2$ M.W. = 173.0	Cl = 41.0%	Chloral ethylalcoholate	3:0860
$\beta,\beta$ -Dichloro- $\alpha$ -hydroxy-isobutyric acid	3:2145	$\alpha,\alpha,\beta$ -Trichloro- <i>n</i> -butyraldehyde hydrate	3:1905
$\beta,\beta'$ -Dichloro- $\alpha$ -hydroxy-isobutyric acid	3:2565	$C_4H_7O_2Cl$ M.W. = 138.6	Cl = 25.6%
$\beta$ -Hydroxyethyl dichloroacetate	3:9107	$\beta$ -Hydroxyethyl chloroacetate	3:6780
$C_4H_7OCl$ M.W. = 100.0	Cl = 33.3%	$\beta$ -Methoxyethyl chloroformate	3:9140
2-Chlorobuten-2-ol-1	3:8240	$C_4H_7OCl_2$ M.W. = 143.0	Cl = 49.6%
3-Chlorobuten-2-ol-1	3:8270	1,3-Dichlorobutanol-2	3:9145
4-Chlorobuten-2-ol-1	3:9114	1,1-Dichloro-2-methylpropanol-2	3:5772
2-Chlorobuten-3-ol-1	3:9113	1,3-Dichloro-2-methylpropanol-2	3:5977
1-Chlorobuten-3-ol-2	3:8110	$\alpha,\alpha'$ -Dichlorodiethyl ether	3:7395
3-Chlorobuten-3-ol-2	3:9115	$\alpha,\beta$ -Dichlorodiethyl ether	3:5640
3-Chloro-2-methylpropen-2-ol-1	3:8340	$\alpha,\beta'$ -Dichlorodiethyl ether	3:9150
$\alpha$ -Chloro- <i>n</i> -butyraldehyde	3:9109	$\beta,\beta'$ -Dichlorodiethyl ether	3:6025
$\beta$ -Chloro- <i>n</i> -butyraldehyde	3:0110	$C_4H_7O_2Cl_2$ M.W. = 159.0	Cl = 41.6%
$\gamma$ -Chloro- <i>n</i> -butyraldehyde	3:9111	Dichloroacetaldehyde ethyl alcoholate	3:5310
$\alpha$ -Chloroisobutyraldehyde	3:7235	$C_4H_7OCl$ M.W. = 108.6	Cl = 32.7%
$\beta$ -Chloroisobutyraldehyde	3:9112	2-Chlorobutanol-1	3:0160
1-Chlorobutanone-2	3:8012	3-Chlorobutanol-1	3:0163
3-Chlorobutanone-2	3:7599	4-Chlorobutanol-1	3:9170
4-Chlorobutanone-2	3:7640	1-Chlorobutanol-2	3:8025
<i>n</i> -Butyryl chloride	3:7370	3-Chlorobutanol-2	3:8000
Isobutyryl chloride	3:7270	<i>d,l</i> -threo-3-Chlorobutanol-2	3:8007
3-Chloro-2-methyl-1,2-epoxypropane	3:7657	<i>d,l</i> -erythro-3-Chlorobutanol-2	3:8001
$\beta$ -Chloroethyl vinyl ether	3:7464	4-Chlorobutanol-2	3:0175
$C_4H_7OCl_2$ M.W. = 177.5	Cl = 59.9%	2-Chloro-2-methylpropanol-1	3:7905
2,2,3-Trichlorobutanol-1	3:1330	3-Chloro-2-methylpropanol-1	3:0150
1,1,1-Trichlorobutanol-2	3:5955	1-Chloro-2-methylpropanol-2	3:7752
1,1,1-Trichloro-2-methylpropanol-2	3:2662	<i>ter</i> -Butyl hypochlorite	3:7165
$C_4H_7O_2Cl$ M.W. = 122.6	Cl = 29.9%	$\alpha$ -Chloroethyl ethyl ether	3:7305
$\alpha$ -Chloro- <i>n</i> -butyric acid	3:9130	$\beta$ -Chloroethyl ethyl ether	3:7463
$\beta$ -Chloro- <i>n</i> -butyric acid	3:0035	$C_4H_7O_2Cl$ M.W. = 124.0	Cl = 29.5%
$\gamma$ -Chloro- <i>n</i> -butyric acid	3:0070	2-( $\beta$ -Chloroethoxy)ethanol-1	3:0153
$\alpha$ -Chloroisobutyric acid	3:0235	3-Chloro-2-methylpropanol-1,2	3:9190
$\beta$ -Chloroisobutyric acid	3:9132	$C_5$ GROUP	
Ethoxyacetyl chloride	3:7745	$C_5H_7O_2Cl_2$ M.W. = 322.8	Cl = 65.9%
$\alpha$ -Chloroethyl acetate	3:7625	Chloralide	3:3510
$\beta$ -Chloroethyl acetate	3:5735	$C_5H_7O_2Cl$ M.W. = 130.5	Cl = 27.2%
1,1,1-Trichloroacetate	3:5700	Furoyl chloride	3:8515
		$C_5H_7O_2Cl_2$ M.W. = 169.0	Cl = 42.0%
		Glutaryl (di)chloride	3:6500
		$C_5H_7OCl$ M.W. = 118.6	Cl = 29.9%
		Tiglyl chloride	3:9210



$C_2H_3O_2Cl$ M.W. = 134.6	Cl = 26.4%	$\beta$ -Chloro- <i>n</i> -valeric acid	3:0270
Ethyl $\alpha$ -chloroacrylate	3:9242	$\gamma$ -Chloro- <i>n</i> -valeric acid	3:9270
Methyl $\alpha$ -chlorocrotonato	3:5870	$\delta$ -Chloro- <i>n</i> -valeric acid	3:0075
Methyl $\beta$ -chlorocrotonate	3:9244	$\alpha$ -Chloro- $\alpha$ -methyl- <i>n</i> -butyric acid	3:8718
Methyl $\beta$ -chloroisocrotonate	3:8028	$\alpha$ -Chloro- $\beta$ -methyl- <i>n</i> -butyric acid	3:0650
$C_6H_7O_2Cl_3$ M.W. = 205.5	Cl = 51.8%	Chloropivalic acid	3:0440
<i>n</i> -Propyl trichloroacetate	3:6135	$\beta$ -Chloro- <i>n</i> -propyl acetate	3:8180
Isopropyl trichloroacetate	3:5975	$\gamma$ -Chloro- <i>n</i> -propyl acetate	3:8310
$C_3H_7O_2Cl$ M.W. = 150.6	Cl = 23.5%	$\beta$ -Chloroisopropyl acetate	3:8150
Carbethoxyacetyl chloride	3:9246	<i>n</i> -Propyl chloroacetate	3:8295
$\beta$ -(Carbomethoxy)propionyl chloride	3:9247	Isopropyl chloroacetate	3:8160
$C_6H_7O_2Cl_2$ M.W. = 221.5	Cl = 48.0%	Ethyl $\alpha$ -chloropropionate	3:8125
$\beta$ -Methoxyethyl trichloroacetate	3:9250	Ethyl $\beta$ -chloropropionate	3:8290
$C_6H_8OCl_2$ M.W. = 155.0	Cl = 45.7%	Methyl $\alpha$ -chloro- <i>n</i> -butyrate	3:8103
$\alpha$ -Chloro- <i>n</i> -valeryl chloride	3:5860	Methyl $\beta$ -chloro- <i>n</i> -butyrate	3:8224
$\gamma$ -Chloro- <i>n</i> -valeryl chloride	3:9260	Methyl $\gamma$ -chloro- <i>n</i> -butyrate	3:8517
$\delta$ -Chloro- <i>n</i> -valeryl chloride	3:9264	Methyl $\alpha$ -chloroisobutyrate	3:7918
$\alpha$ -Chloro- $\alpha$ -methyl- <i>n</i> -butyryl chloride	3:5670	<i>n</i> -Butyl chloroformate	3:7980
$\alpha$ -Chloro- $\beta$ -methyl- <i>n</i> -butyryl chloride	3:8144	Isobutyl chloroformate	3:7760
Chloropivalyl chloride	3:9266	$C_6H_9O_2Cl$ M.W. = 152.6	Cl = 23.2%
$C_6H_9O_2Cl_2$ M.W. = 171.0	Cl = 41.5%	Glycerol $\alpha$ -chlorohydrin $\alpha'$ -acetate	3:0775
$\beta, \gamma$ -Dichloro- <i>n</i> -propyl acetate	3:6220	Glycerol $\alpha$ -chlorohydrin $\beta$ -acetate	3:6517
$\beta, \beta'$ -Dichloroisopropyl acetate	3:6318	Glycerol $\beta$ -chlorohydrin $\alpha$ -acetate	3:6618
<i>n</i> -Propyl dichloroacetate	3:6000	$\beta$ -Methoxyethyl chloroacetate	3:9285
Isopropyl dichloroacetate	3:5890	$\beta$ -Ethoxyethyl chloroformate	3:0290
Ethyl $\alpha, \beta$ -dichloropropionate	3:6090	$C_6H_{11}OCl$ M.W. = 122.6	Cl = 28.0%
$C_6H_9O_2Cl_2$ M.W. = 187.0	Cl = 37.9%	5-Chloropentanol-1	3:9295
Di-( $\beta$ -chloroethyl) carbonate	3:6790	1-Chloropentanol-2	3:8225
$C_6H_9OCl$ M.W. = 120.6	Cl = 29.4%	1-Chloropentanol-3	3:8500
1-Chloropentanone-2	3:8217	1-Chloro-2-methylbutanol-2	3:8175
3-Chloropentanone-2	3:7893	3-Chloro-2-methylbutanol-2	3:8030
4-Chloropentanone-2	3:8243	4-Chloro-2-methylbutanol-2	3:8335
5-Chloropentanone-2	3:9267	2-Chloro-2-methylbutanol-2	3:8335
1-Chloropentanone-3	3:9268	2-Chloro-2-methylbutanol-2	3:8335
2-Chloropentanone-3	3:7935	2-Chloro-2-methylbutanol-2	3:8335
1-Chloro-2-methylbutanone-3	3:8217	2-Chloro-2-methylbutanol-2	3:8335
2-Chloro-2-methylbutanone-3	3:7893	2-Chloro-2-methylbutanol-2	3:8335
<i>n</i> -Valeryl chloride	3:5860	2-Chloro-2-methylbutanol-2	3:8335
$\alpha$ -Methyl- <i>n</i> -butyryl chloride	3:8144	2-Chloro-2-methylbutanol-2	3:8335
$\beta$ -Methyl- <i>n</i> -butyryl chloride	3:8517	2-Chloro-2-methylbutanol-2	3:8335
$\alpha, \alpha$ -Dimethylpropionyl chloride	3:5670	2-Chloro-2-methylbutanol-2	3:8335
Tetrahydro- $\alpha$ -furfuryl chloride	3:8144	2-Chloro-2-methylbutanol-2	3:8335
$C_6H_9O_2Cl$ M.W. = 130.6	Cl = 23.5%	2-Chloro-2-methylbutanol-2	3:8335
$\alpha$ -Chloro- <i>n</i> -valeric acid	3:0270	2-Chloro-2-methylbutanol-2	3:8335

$C_6H_2O_2Cl_2$ M.W. = 177.0	Cl = 40.1%	2-Chlorohydroquinone	3:3130
2,3-Dichlorobenzoquinone-1,4	3:2355		
2,5-Dichlorobenzoquinone-1,4	3:4470	$C_6H_7O_4Cl$ M.W. = 178.6	Cl = 19.9%
2,6-Dichlorobenzoquinone-1,4	3:3750	Dimethyl chlorofumarate	3:6582
		Dimethyl chloromaleate	3:9351
$C_6H_2O_2Cl_4$ M.W. = 217.9	Cl = 57.2%		
Tetrachloropyrocatechol	3:4975	$C_6H_4O_2Cl_2$ M.W. = 183.0	Cl = 38.7%
Tetrachlororesorcinol	3:4135	Adipyl (di)chloride	3:9352
Tetrachlorohydroquinone	3:4941		
$C_6H_2O_4Cl_2$ M.W. = 209.0	Cl = 33.9%	$C_6H_4O_4Cl_2$ M.W. = 215.0	Cl = 33.0%
2,5-Dichloro-3,6-dihydroxybenzoquinone-1,4	3:4970	Di-( $\beta$ -chloroethyl) oxalate	3:0572
		Ethylene glycol bis-(chloroacetate)	3:0720
$C_6H_2OCl_4$ M.W. = 197.5	Cl = 53.9%	Dimethyl <i>d,l</i> - $\alpha,\alpha'$ -dichlorosuccinate	3:0485
2,3,4-Trichlorophenol	3:2185	Dimethyl <i>meso</i> - $\alpha,\alpha'$ -dichlorosuccinate	3:0210
2,3,5-Trichlorophenol	3:1340		
2,3,6-Trichlorophenol	3:1160	$C_6H_5OCl$ M.W. = 132.6	Cl = 26.7%
2,4,5-Trichlorophenol	3:1620	2-Chlorocyclohexanone-1	3:0120
2,4,6-Trichlorophenol	3:1673	3-Chlorocyclohexanone-1	3:9360
3,4,5-Trichlorophenol	3:2885	4-Chlorocyclohexanone-1	3:0364
$C_6H_4O_2Cl$ M.W. = 142.5	Cl = 24.0%		
2-Chlorobenzoquinone-1,4	3:1100	$C_6H_5O_2Cl$ M.W. = 148.6	Cl = 23.9%
$C_6H_2O_2Cl_3$ M.W. = 213.5	Cl = 49.8%	Ethyl $\alpha$ -chlorocrotonate	3:8523
3,4,5-Trichlorocatechol	3:3448	Ethyl $\beta$ -chlorocrotonate	3:8538
2,4,6-Trichlororesorcinol	3:2174	Ethyl $\gamma$ -chlorocrotonate	3:8657
2,3,5-Trichlorohydroquinone	3:4032		
$C_6H_2O_2Cl_4$ M.W. = 229.5	Cl = 40.4%	Ethyl $\alpha$ -chloroisocrotonate	3:9363
4,5,6-Trichloropyrogallol	3:4782	Ethyl $\beta$ -chloroisocrotonate	3:8323
3,5,6-Trichloro-2-hydroxyhydroquinone	3:4444		
2,4,6-Trichlorophloroglucinol	3:4030	$C_6H_5O_2Cl_2$ M.W. = 210.5	Cl = 48.0%
$C_6H_4OCl_2$ M.W. = 163.0	Cl = 43.5%	$\beta,\beta,\beta$ -Trichloro- <i>tert</i> -butylacetate	3:6180
2,3-Dichlorophenol	3:1176	Ethyl $\alpha,\alpha,\beta$ -trichloro- <i>n</i> -butyrate	3:6350
2,4-Dichlorophenol	3:0560		
2,5-Dichlorophenol	3:1190	<i>n</i> -Butyl trichloroacetate	3:6315
2,6-Dichlorophenol	3:1595	<i>sec</i> -Butyl trichloroacetate	3:9372
3,4-Dichlorophenol	3:1460	Isobutyl trichloroacetate	3:0140
3,5-Dichlorophenol	3:1670	<i>tert</i> -Butyl trichloroacetate	3:0139
$C_6H_4O_2Cl_3$ M.W. = 179.0	Cl = 39.6%	$C_6H_5O_2Cl$ M.W. = 164.0	Cl = 21.5%
3,5-Dichlorocatechol	3:2192	$\gamma$ -(Carbomethoxy)- <i>n</i> -butyryl chloride	3:9373
4,5-Dichlorocatechol	3:3525		
4,6-Dichlororesorcinol	3:3350	Ethyl $\alpha$ -chloroacetoacetate	3:6207
2,3-Dichlorohydroquinone	3:4220	Ethyl $\gamma$ -chloroacetoacetate	3:6375
2,5-Dichlorohydroquinone	3:4690		
2,6-Dichlorohydroquinone	3:4600	$C_6H_5O_2Cl_4$ M.W. = 235.5	Cl = 45.2%
$C_6H_4OCl$ M.W. = 128.6	Cl = 27.6%	Trichloroparaldehyde	3:2300
<i>o</i> -Chlorophenol	3:5950	$C_{11}H_{14}OCl$ M.W. = 131.0	Cl = 26.3%
<i>m</i> -Chlorophenol	3:0253	2-Chlorocyclohexanol-1	
<i>p</i> -Chlorophenol	3:0175	Liquid stereoisomer ( <i>cis</i> )	3:9374
		Solid stereoisomer ( <i>trans</i> )	3:0175
$C_6H_5O_2Cl$ M.W. = 141.6	Cl = 21.5%	4-Chlorocyclohexanol-1	3:9376
3-Chlorocatechol	3:0745		
4-Chlorocatechol	3:2170	<i>n</i> -Caproyl chloride	3:8169
2-Chlororesorcinol	3:3690		
4-Chlororesorcinol	3:3160	$\alpha$ -Methyl- <i>n</i> -valeryl chloride	3:8070
5-Chlororesorcinol	3:3230	$\beta$ -Methyl- <i>n</i> -valeryl chloride	3:8035
		$\gamma$ -Methyl- <i>n</i> -valeryl chloride	3:8090

$\alpha,\alpha$ -Dimethyl- <i>n</i> -butyryl chloride	3:7900	<b>C<sub>7</sub> GROUP</b>	
$\alpha,\beta$ -Dimethyl- <i>n</i> -butyryl chloride	3:7965	$C_7HOCl_4$	M.W.=278.4
$\beta,\beta$ -Dimethyl- <i>n</i> -butyryl chloride	3:7890	Pentachlorobenzaldehyde	Cl=63.7% 3:4892
$\alpha$ -Ethyl- <i>n</i> -butyryl chloride	3:7990	$C_7HO_2Cl_5$	M.W.=294.4
$C_6H_{11}O_2Cl$	M.W.=150.6	Pentachlorobenzoic acid	Cl=60.2% 3:4910
<i>n</i> -Butyl chloroacetate	3:8530	$C_7H_2OCl_4$	M.W.=243.9
<i>sec</i> -Butyl chloroacetate	3:8350	2,3,4,5-Tetrachlorobenzaldehyde	Cl=58.1% 3:3140
<i>ter</i> -Butyl chloroacetate	3:8220	2,3,4,6-Tetrachlorobenzaldehyde	3:2700
Isobutyl chloroacetate	3:8375	2,3,5,6-Tetrachlorobenzaldehyde	3:2700
<i>n</i> -Propyl $\alpha$ -chloropropionate	3:9384	$C_7H_2O_2Cl_4$	M.W.=259.9
Isopropyl $\alpha$ -chloropropionate	3:8165	2,3,4,5-Tetrachlorobenzoic acid	Cl=54.6% 3:4790
<i>n</i> -Propyl $\beta$ -chloropropionate	3:8545	$C_7H_3OCl_3$	M.W.=209.5
Isopropyl $\beta$ -chloropropionate	3:9388	2,3,4-Trichlorobenzaldehyde	Cl=50.8% 3:2445
Ethyl $\alpha$ -chloro- <i>n</i> -butyrate	3:8307	2,3,5-Trichlorobenzaldehyde	3:1060
Ethyl $\beta$ -chloro- <i>n</i> -butyrate	3:8373	2,3,6-Trichlorobenzaldehyde	3:2287
Ethyl $\gamma$ -chloro- <i>n</i> -butyrate	3:8597	2,4,5-Trichlorobenzaldehyde	3:3375
Ethyl $\alpha$ -chloroisobutyrate	3:8147	2,4,6-Trichlorobenzaldehyde	3:1200
Methyl $\alpha$ -chloro- <i>n</i> -valerate	3:8264	3,4,5-Trichlorobenzaldehyde	3:2440
<i>n</i> -Amyl chloroformate	3:9380	$C_7H_3O_2Cl_3$	M.W.=225.4
Isoamyl chloroformate	3:8215	2,4,6-Trichloro-3-hydroxybenzaldehyde	Cl=47.2% 3:3530
$C_6H_{11}O_2Cl_3$	M.W.=221.5	2,3,4-Trichlorobenzoic acid	3:4910
Chloral diethylacetal	3:6317	2,3,5-Trichlorobenzoic acid	3:4185
Chloral <i>n</i> -butylalcoholate	3:0843	2,3,6-Trichlorobenzoic acid	3:4500
$C_6H_{11}O_4Cl$	M.W.=182.6	2,4,5-Trichlorobenzoic acid	3:4630
Diethylene glycol mono-(chloroacetate)	3:9390	2,4,6-Trichlorobenzoic acid	3:4545
$C_6H_{11}OCl_2$	M.W.=171.1	3,4,5-Trichlorobenzoic acid	3:4920
$\beta,\beta'$ -Dichloro-di- <i>n</i> -propyl ether	3:8610	$C_7H_5OCl_2$	M.W.=175.0
$\gamma,\gamma'$ -Dichloro-di- <i>n</i> -propyl ether	3:8745	2,3-Dichlorobenzaldehyde	Cl=40.5% 3:1480
$\beta,\beta'$ -Dichloro-di-isopropyl ether	3:8605	2,4-Dichlorobenzaldehyde	3:1800
$C_6H_{11}O_2Cl_2$	M.W.=187.1	2,5-Dichlorobenzaldehyde	3:1145
Formaldehyde $\beta,\beta'$ -dichloro-isopropyl ethylacetal	3:9394	2,6-Dichlorobenzaldehyde	3:1690
Acetaldehyde bis-( $\beta$ -chloroethyl) acetal	3:6210	3,4-Dichlorobenzaldehyde	3:0550
Dichloroacetaldehyde diethylacetal	3:6110	3,5-Dichlorobenzaldehyde	3:1475
Ethylene glycol bis-( $\beta$ -chloroethyl) ether	3:6655	<i>o</i> -Chlorobenzoyl chloride	3:6640
$C_6H_{11}OCl$	M.W.=136.6	<i>m</i> -Chlorobenzoyl chloride	3:6590
6-Chlorohexanol-1	3:9395	<i>p</i> -Chlorobenzoyl chloride	3:6550
<i>n</i> -Butyl $\alpha$ -chloroethyl ether	3:9396	$C_7H_4O_2Cl_2$	M.W.=191.0
$C_6H_{11}O_2Cl$	M.W.=152.6	3,5-Dichloro-2-hydroxybenzaldehyde	Cl=37.1% 3:2637
Chloroacetaldehyde diethylacetal	3:8228	2,4-Dichloro-3-hydroxybenzaldehyde	3:4140
		2,6-Dichloro-3-hydroxybenzaldehyde	3:4160
		4,6-Dichloro-3-hydroxybenzaldehyde	3:3952
		3,5-Dichloro-4-hydroxybenzaldehyde	3:4400

2,3-Dichlorobenzoic acid	3:4650	2,6-Dichloro-4-methylphenol	3:0400
2,4-Dichlorobenzoic acid	3:4560	$C_7H_7OCl$ M.W. = 142.6	Cl = 24.9%
2,5-Dichlorobenzoic acid	3:4340	3-Chloro-2-methylphenol	3:2280
2,6-Dichlorobenzoic acid	3:4200	4-Chloro-2-methylphenol	3:0780
3,4-Dichlorobenzoic acid	3:4925	5-Chloro-2-methylphenol	3:1815
3,5-Dichlorobenzoic acid	3:4840	6-Chloro-2-methylphenol	3:8015
$C_7H_4O_3Cl_2$ M.W. = 207.0	Cl = 34.3%	2-Chloro-3-methylphenol	3:1055
3,5-Dichloro-2-hydroxybenzoic acid	3:4935	4-Chloro-3-methylphenol	3:1535
3,5-Dichloro-4-hydroxybenzoic acid	3:4950	6-Chloro-3-methylphenol	3:0700
$C_7H_7OCl$ M.W. = 140.6	Cl = 25.2%	2-Chloro-4-methylphenol	3:6215
<i>o</i> -Chlorobenzaldehyde	3:6410	3-Chloro-4-methylphenol	3:1025
<i>m</i> -Chlorobenzaldehyde	3:6475	Phenoxymethyl chloride	3:9448
<i>p</i> -Chlorobenzaldehyde	3:0765	<i>o</i> -Chloroanisole	3:6255
Benzoyl chloride	3:6240	<i>m</i> -Chloroanisole	3:6195
$C_7H_5OCl_3$ M.W. = 211.5	Cl = 50.3%	<i>p</i> -Chloroanisole	3:6300
2,4,6-Trichloro-3-methylphenol	3:0618	$C_7H_{10}O_2Cl_2$ M.W. = 197.1	Cl = 36.0%
$C_7H_5O_2Cl$ M.W. = 156.5	Cl = 22.7%	Pimelyl (di)chloride	3:9450
3-Chloro-2-hydroxybenzaldehyde	3:1010	$C_7H_{11}OCl$ M.W. = 146.6	Cl = 24.2%
4-Chloro-2-hydroxybenzaldehyde	3:0960	Hexahydrobenzoyl chloride	3:8580
5-Chloro-2-hydroxybenzaldehyde	3:2800	$C_7H_{11}O_2Cl$ M.W. = 162.6	Cl = 21.8%
2-Chloro-3-hydroxybenzaldehyde	3:4085	Cyclohexyl chloroformate	3:5770
4-Chloro-3-hydroxybenzaldehyde	3:3780	$C_7H_{11}O_2Cl_3$ M.W. = 233.5	Cl = 45.0%
6-Chloro-3-hydroxybenzaldehyde	3:3350	<i>n</i> -Amyl trichloroacetate	3:6560
2-Chloro-4-hydroxybenzaldehyde	3:4280	Isoamyl trichloroacetate	3:6490
3-Chloro-4-hydroxybenzaldehyde	3:4065	<i>ter</i> -Amyl trichloroacetate	3:6185
<i>o</i> -Chlorobenzoic acid	3:4150	$C_7H_{11}O_4Cl$ M.W. = 194.6	Cl = 18.2%
<i>m</i> -Chlorobenzoic acid	3:4392	3-Chloropropanediol-1,2 diacetate	3:6840
<i>p</i> -Chlorobenzoic acid	3:4940	$C_7H_{11}O_2Cl_2$ M.W. = 215.1	Cl = 33.0%
<i>o</i> -Hydroxybenzoyl chloride	3:0085	Di-( $\gamma$ -chloro- <i>n</i> -propyl) carbonate	3:6895
<i>m</i> -Hydroxybenzoyl chloride	3:9446	$C_7H_{11}OCl$ M.W. = 148.6	Cl = 23.9%
<i>p</i> -Hydroxybenzoyl chloride	3:9447	<i>n</i> -Heptanoyl chloride	3:8520
$C_7H_5O_2Cl$ M.W. = 172.6	Cl = 20.6%	$\alpha$ -Methyl- <i>n</i> -caproyl chloride	3:0452
3-Chloro-2-hydroxybenzoic acid	3:4745	$\beta$ -Methyl- <i>n</i> -caproyl chloride	3:8305
4-Chloro-2-hydroxybenzoic acid	3:4908	$\gamma$ -Methyl- <i>n</i> -caproyl chloride	3:8355
5-Chloro-2-hydroxybenzoic acid	3:4705	$\delta$ -Methyl- <i>n</i> -caproyl chloride	3:8365
6-Chloro-2-hydroxybenzoic acid	3:4610	$\alpha,\alpha$ -Dimethyl- <i>n</i> -valeryl chloride	3:9456
2-Chloro-3-hydroxybenzoic acid	3:4395	$\alpha,\beta$ -Dimethyl- <i>n</i> -valeryl chloride	3:9458
4-Chloro-3-hydroxybenzoic acid	3:4933	$\gamma,\gamma$ -Dimethyl- <i>n</i> -valeryl chloride	3:9460
6-Chloro-3-hydroxybenzoic acid	3:4720	$\alpha$ -Ethyl- <i>n</i> -valeryl chloride	3:8235
2-Chloro-4-hydroxybenzoic acid	3:4430	$\alpha,\alpha,\beta$ -Trimethyl- <i>n</i> -butyryl chloride	3:8145
3-Chloro-4-hydroxybenzoic acid	3:4675	$\alpha$ -Ethyl- $\beta$ -methyl- <i>n</i> -butyryl chloride	3:0462
$C_7H_7OCl_2$ M.W. = 177.0	Cl = 40.1%	$C_7H_{13}O_2Cl$ M.W. = 164.6	Cl = 21.5%
4,5-Dichloro-2-methylphenol	3:2310	<i>n</i> -Butyl $\alpha$ -chloropropionate	3:8595
4,6-Dichloro-2-methylphenol	3:1070	Isobutyl $\alpha$ -chloropropionate	3:9470
2,4-Dichloro-3-methylphenol	3:1205		
2,6-Dichloro-3-methylphenol	3:0150		
4,6-Dichloro-3-methylphenol	3:1745		

*n*-Butyl  $\beta$ -chloropropionate 3:8474  
 Isobutyl  $\beta$ -chloropropionate 3:8635  
 Ethyl  $\alpha$ -chloro-*n*-valerate 3:8596  
 Ethyl  $\beta$ -chloro-*n*-valerate 3:8629  
 Ethyl  $\gamma$ -chloro-*n*-valerate 3:8703  
 Ethyl  $\delta$ -chloro-*n*-valerate 3:8727

Ethyl  $\alpha$ -chloroisovalerate 3:8523

Ethyl  $\alpha$ -chloro- $\alpha$ -methyl-*n*-butyrate 3:8518

$C_7H_{11}OCl$  M.W. = 150.7 Cl = 23.5%  
 7-Chloroheptanol-1 3:0013  
*n*-Amyl  $\alpha$ -chloroethyl ether 3:9480

$C_7H_{11}O_2Cl$  M.W. = 166.7 Cl = 21.3%  
 $\beta$ -Chloropropionaldehyde diethylacetal 3:9490

### C<sub>2</sub> GROUP

$C_2H_2O_3Cl_2$  M.W. = 217.0 Cl = 32.7%  
 3,4-Dichlorophthalic anhydride 3:3695  
 3,5-Dichlorophthalic anhydride 3:2375  
 3,6-Dichlorophthalic anhydride 3:4860  
 4,5-Dichlorophthalic anhydride 3:4830

$C_2H_2O_4Cl_4$  M.W. = 303.9 Cl = 46.7%  
 Tetrachlorophthalic acid 3:4946

$C_2H_2O_3Cl$  M.W. = 182.6 Cl = 19.4%  
 3-Chlorophthalic anhydride 3:3909  
 4-Chlorophthalic anhydride 3:2725

$C_2H_2O_3Cl_2$  M.W. = 203.0 Cl = 34.9%  
 Phthalyl (di)chloride (*sym.*) 3:6900  
 Phthalyl (di)chloride (*unsym.*) 3:2395

Isophthalyl (di)chloride 3:0520

Terephthalyl (di)chloride 3:2205

$C_2H_2O_4Cl_2$  M.W. = 235.0 Cl = 30.2%  
 3,4-Dichlorophthalic acid 3:4380  
 3,5-Dichlorophthalic acid 3:4580  
 3,6-Dichlorophthalic acid 3:4870  
 4,5-Dichlorophthalic acid 3:4890

4,6-Dichloroisophthalic acid 3:4965

2,5-Dichloroterephthalic acid 3:4935

$C_2H_2OCl_4$  M.W. = 223.5 Cl = 47.6%  
 $\omega,\omega,\omega$ -Trichloroacetophenone 3:6874

$C_2H_2O_2Cl$  M.W. = 184.6 Cl = 19.2%  
 Piperonyl chloride 3:1960

$C_2H_2O_3Cl_3$  M.W. = 255.6 Cl = 41.6%  
 2,4,5-Trichlorophenoxyacetic acid 3:4335

$C_2H_2O_4Cl$  M.W. = 200.6 Cl = 17.7%  
 3-Chlorophthalic acid 3:4820  
 4-Chlorophthalic acid 3:4390

4-Chloroisophthalic acid 3:4980  
 5-Chloroisophthalic acid 3:4960

Chloroterephthalic acid 3:4995

$C_2H_2OCl_2$  M.W. = 189.0 Cl = 37.5%  
 $\omega,\omega$ -Dichloroacetophenone 3:6835

*p*-Chlorophenacyl chloride 3:2990

$C_2H_2O_2Cl_2$  M.W. = 221.0 Cl = 32.1%  
 2,4-Dichlorophenoxyacetic acid 3:4095

$C_2H_7OCl$  M.W. = 154.6 Cl = 22.9%  
 $\omega$ -Chloroacetophenone 3:1212  
 $o$ -Chloroacetophenone 3:6615  
 $m$ -Chloroacetophenone 3:6815  
 $p$ -Chloroacetophenone 3:6735

Phenylacetyl chloride 3:9567

*o*-Tolyl chloride 3:8740  
*m*-Tolyl chloride 3:6535  
*p*-Tolyl chloride 3:6600

$C_2H_2OCl_3$  M.W. = 225.5 Cl = 47.2%  
 4,5,6-Trichloro-2,3-dimethylphenol 3:4743  
 3,5,6-Trichloro-2,4-dimethylphenol 3:4707  
 3,4,6-Trichloro-2,5-dimethylphenol 3:4709  
 2,5,6-Trichloro-3,4-dimethylphenol 3:4747  
 2,4,6-Trichloro-3,5-dimethylphenol 3:4713

$C_2H_2O_2Cl$  M.W. = 170.6 Cl = 20.8%  
 3-Chloro-2-methylbenzoic acid 3:4435  
 4-Chloro-2-methylbenzoic acid 3:4700  
 5-Chloro-2-methylbenzoic acid 3:4670  
 6-Chloro-2-methylbenzoic acid 3:3275

4-Chloro-3-methylbenzoic acid 3:4915  
 5-Chloro-3-methylbenzoic acid 3:4715  
 6-Chloro-3-methylbenzoic acid 3:4615

2-Chloro-4-methylbenzoic acid 3:4355  
 3-Chloro-4-methylbenzoic acid 3:4900

2-Chlorophenylacetic acid 3:2640  
 3-Chlorophenylacetic acid 3:1910  
 4-Chlorophenylacetic acid 3:3135

Phenoxyacetyl chloride 3:8790

2-Methoxybenzoyl chloride 3:6870  
 3-Methoxybenzoyl chloride 3:6797  
 4-Methoxybenzoyl chloride 3:6890

Phenyl chloroacetate 3:0565

Benzyl chloroformate 3:9565

Methyl <i>o</i> -chlorobenzoate	3:6695	$C_8H_7O_2Cl$	M.W. = 226.7	Cl = 15.0%
Methyl <i>m</i> -chlorobenzoate	3:6670	Triethyl glycol mono- (chloroacetate)		3:9598
Methyl <i>p</i> -chlorobenzoate	3:0535	$C_8H_7OCl$	M.W. = 164.7	Cl = 21.5%
$C_8H_7O_2Cl$	M.W. = 186.6	8-Chloro-octanol-1		3:9590
<i>o</i> -Chlorophenoxyacetic acid	3:4260	$C_8H_{11}O_2Cl$	M.W. = 180.7	Cl = 19.6%
<i>m</i> -Chlorophenoxyacetic acid	3:3325	$\beta$ -Chloro- <i>n</i> -butyraldehyde diethylacetal		3:9594
<i>p</i> -Chlorophenoxyacetic acid	3:4375			
$C_6H_4OCl_2$	M.W. = 191.1			
5,6-Dichloro-2,3-dimethylphenol	3:2442	<b>C<sub>9</sub> GROUP</b>		
2,5-Dichloro-3,4-dimethylphenol	3:2216	$C_9H_9OCl$	M.W. = 164.6	Cl = 21.5%
2,6-Dichloro-3,4-dimethylphenol	3:0935	Phenylpropionyl chloride		3:9639
5,6-Dichloro-3,4-dimethylphenol	3:3095	$C_9H_7O_2Cl$	M.W. = 180.6	Cl = 19.6%
2,4-Dichloro-3,5-dimethylphenol	3:2192	<i>o</i> -Chlorophenylpropionic acid		3:3956
2,6-Dichloro-3,5-dimethylphenol	3:2633	<i>m</i> -Chlorophenylpropionic acid		3:4102
$C_9H_9OCl$	M.W. = 156.6	<i>p</i> -Chlorophenylpropionic acid		3:4265
Chloromethyl-phenyl-carbinol	3:9570	$C_9H_7O_2Cl$	M.W. = 244.6	Cl = 14.4%
4-Chloro-2,3-dimethylphenol	3:2218	5-Chlorobenzenetricarboxylic acid-1,2,4		3:4855
5-Chloro-2,3-dimethylphenol	3:2115	2-Chlorobenzenetricarboxylic acid-1,3,5		3:4975
5-Chloro-2,4-dimethylphenol	3:2460	$C_9H_7OCl$	M.W. = 166.6	Cl = 21.3%
6-Chloro-2,4-dimethylphenol	3:8784	Cinnamoyl chloride		3:0330
4-Chloro-2,5-dimethylphenol	3:1922	$C_9H_7OCl$	M.W. = 168.6	Cl = 21.0%
4-Chloro-2,6-dimethylphenol	3:2180	$\omega$ -Chloro- <i>o</i> -methylacetophenone		3:9660
2-Chloro-3,4-dimethylphenol	3:0188	$\omega$ -Chloro- <i>p</i> -methylacetophenone		3:1130
5-Chloro-3,4-dimethylphenol	3:2705	$\alpha$ -Chloroethyl phenyl ketone		3:9664
6-Chloro-3,4-dimethylphenol	3:1754	$\beta$ -Chloroethyl phenyl ketone		3:1115
2-Chloro-3,5-dimethylphenol	3:0944	<i>p</i> -Chlorophenyl ethyl ketone		3:0340
4-Chloro-3,5-dimethylphenol	3:3505	Hydrocinnamoyl chloride		3:8787
$\beta$ -Phenoxyethyl chloride	3:0165	$C_9H_7O_2Cl$	M.W. = 184.6	Cl = 19.2%
<i>o</i> -Chlorophenetole	3:8735	Ethyl <i>o</i> -chlorobenzoate		3:6400
<i>m</i> -Chlorophenetole	3:6323	Ethyl <i>m</i> -chlorobenzoate		3:0770
<i>p</i> -Chlorophenetole	3:0090	Ethyl <i>p</i> -chlorobenzoate		3:6756
$C_{10}H_8O_4Cl$	M.W. = 206.6	$\beta$ -Chloroethyl benzoate		3:8560
Diethyl chlorofumarate	3:6464	$C_9H_9OCl$	M.W. = 170.6	Cl = 20.8%
Diethyl chloromaleate	3:6637	$\gamma$ -Phenoxy- <i>n</i> -propyl chloride		3:6520
$C_{10}H_8O_4Cl_2$	M.W. = 211.1	$C_{10}H_7O_2Cl_2$	M.W. = 225.1	Cl = 31.5%
Fuleryl (di)chloride	3:9576	Asclayl (di)chloride		3:9640
$C_{10}H_8O_4Cl_2$	M.W. = 243.1	$C_{10}H_7OCl$	M.W. = 176.7	Cl = 20.1%
Diethyl di- <i>o,o'</i> -dichlorosuccinate	3:8579	Pelargonyl chloride		3:8765
Diethyl meso- <i>o,o'</i> -dichlorosuccinate	3:1564	$C_{10}H_{11}OCl$	M.W. = 178.7	Cl = 19.5%
$C_{10}H_9OCl$	M.W. = 162.7	9-Chlorononanol-1		3:0170
$\alpha$ -Octanoyl chloride	3:6640			
$C_{10}H_{11}O_2Cl$	M.W. = 178.7	<b>C<sub>10</sub> GROUP</b>		
Isomyl $\alpha$ -chloropropionate	3:9150	$C_{10}H_{11}O_2Cl_2$	M.W. = 191.6	Cl = 18.5%
Isomyl $\beta$ -chloropropionate	3:9720	3,4-Dichlorosaphthoquinone-1,2		3:4773
		2,3-Dichlorosaphthoquinone-1,4		3:4427

$C_{10}H_6O_2Cl$ M.W. = 192.6	Cl = 18.4%	$C_{10}H_{14}O_2Cl_2$ M.W. = 239.1	Cl = 29.7%
3-Chloronaphthoquinone-1,2	3:4704	Sebacyl (di)chloride	3:9780
4-Chloronaphthoquinone-1,2	3:4000		
2-Chloronaphthoquinone-1,4	3:3580	$C_{10}H_{19}OCl$ M.W. = 190.7	Cl = 18.6%
5-Chloronaphthoquinone-1,4	3:4492	<i>n</i> -Decanoyl chloride	3:8890
6-Chloronaphthoquinone-1,4	3:3145		
$C_{10}H_8OCl_2$ M.W. = 213.1	Cl = 33.3%	$C_{10}H_{21}OCl$ M.W. = 192.6	Cl = 18.4%
2,3-Dichloronaphthol-1	3:2935	10-Chlorodecanol-1	3:0014
2,4-Dichloronaphthol-1	3:3250	$C_{11}H_7OCl$ M.W. = 190.6	Cl = 18.6%
5,7-Dichloronaphthol-1	3:3985	$\alpha$ -Naphthoyl chloride	3:6930
5,8-Dichloronaphthol-1	3:3420	$\beta$ -Naphthoyl chloride	3:0900
6,7-Dichloronaphthol-1	3:4315		
7,8-Dichloronaphthol-1	3:2635	$C_{11}H_{17}O_2Cl$ M.W. = 206.6	Cl = 17.2%
1,3-Dichloronaphthol-2	3:1990	2-Chloronaphthoic acid-1	3:4330
1,4-Dichloronaphthol-2	3:3840	4-Chloronaphthoic acid-1	3:4936
1,6-Dichloronaphthol-2	3:3600	5-Chloronaphthoic acid-1	3:4944
3,4-Dichloronaphthol-2	3:3295	6-Chloronaphthoic acid-1	3:4845
4,8-Dichloronaphthol-2	3:4420	7-Chloronaphthoic acid-1	3:4942
5,8-Dichloronaphthol-2	3:4155	8-Chloronaphthoic acid-1	3:4680
$C_{10}H_7OCl$ M.W. = 178.6	Cl = 19.8%	1-Chloronaphthoic acid-2	3:4885
2-Chloronaphthol-1	3:1490	3-Chloronaphthoic acid-2	3:4928
3-Chloronaphthol-1	3:4170	5-Chloronaphthoic acid-2	3:4952
4-Chloronaphthol-1	3:3720	8-Chloronaphthoic acid-2	3:4948
5-Chloronaphthol-1	3:3960		
6-Chloronaphthol-1	3:2015	$C_{11}H_{19}O_2Cl$ M.W. = 234.7	Cl = 15.1%
7-Chloronaphthol-1	3:3810	$\omega$ -(Carbomethoxy)pelargonyl chloride	3:9793
8-Chloronaphthol-1	3:1610		
1-Chloronaphthol-2	3:1700	$C_{11}H_{21}OCl$ M.W. = 204.7	Cl = 17.3%
3-Chloronaphthol-2	3:2545	Undecanoyl chloride	3:9880
4-Chloronaphthol-2	3:3045		
5-Chloronaphthol-2	3:3945	<b><math>C_{12}</math> GROUP</b>	
6-Chloronaphthol-2	3:3500	$C_{12}H_9OCl$ M.W. = 204.7	Cl = 17.3%
7-Chloronaphthol-2	3:3925	3-Chloro-2-hydroxyhiphenyl	3:1757
8-Chloronaphthol-2	3:2965	5-Chloro-2-hydroxyhiphenyl	3:8980
$C_{12}H_{11}OCl$ M.W. = 182.6	Cl = 19.4%	3-Chloro-4-hydroxyhiphenyl	3:1900
$\omega$ -Chloro-2,4-dimethyl-acetophenone	3:1355	4'-Chloro-4-hydroxyhiphenyl	3:4262
$\omega$ -Chloro-2,5-dimethyl-acetophenone	3:0245	$\alpha$ -Naphthylacetyl chloride	3:9856
$\omega$ -Chloro-3,4-dimethyl-acetophenone	3:1775		
2,4,6-Trimethylbenzoyl chloride	3:9750	$C_{12}H_{21}O_2Cl$ M.W. = 319.7	Cl = 33.3%
$C_{12}H_{15}OCl$ M.W. = 184.7	Cl = 19.2%	Para-( $\beta$ -chloro- <i>n</i> -butyraldehyde)	3:2650
2-Chloro-4- <i>n</i> -butylphenol	3:8530	Para-( $\alpha$ -chloro-isobutyraldehyde)	3:3220
2-Chloro-4- <i>ter</i> -butylphenol	3:9760	$C_{12}H_{25}OCl$ M.W. = 218.8	Cl = 16.2%
<i>p</i> -Chlorocarvacrol	3:0480	Lauryl chloride	3:9858
<i>p</i> -Chlorothymol	3:1293	$C_{12}H_{23}OCl$ M.W. = 220.8	Cl = 16.1%
$C_{12}H_{19}O_2Cl$ M.W. = 200.7	Cl = 17.7%	12-Chlorododecanol-1	3:0172
$\beta$ -Chloroethyl $\beta'$ -phenoxyethyl ether	3:9770		
		<b><math>C_{13}</math> GROUP</b>	
		$C_{13}H_{17}OCl_2$ M.W. = 251.1	Cl = 28.2%
		2,2'-Dichlorobenzophenone	3:0717
		2,3'-Dichlorobenzophenone	3:9859-A
		2,4-Dichlorobenzophenone	3:0825
		2,4'-Dichlorobenzophenone	3:1565
		2,5-Dichlorobenzophenone	3:2340
		2,6-Dichlorobenzophenone	3:2235

(111) *Chem. Abstr.* 1927, 1415-1417 Feb. 20, 1927; *Cent.* 1927, II 1800. (112) Williams, *J. Am. Chem. Soc.* 65, 1927, 1111. (113) Federal Phosphor Co. (to Swann Research, Inc.), *U.S. Pat.* 2,140,000 (1938). (114) *Chem. Abstr.* 1938, 1400-1401 (1938). (115) *Chem. Abstr.* 1938, 1400-1401 (1938). (116) *Chem. Abstr.* 1938, 1400-1401 (1938). (117) *Chem. Abstr.* 1938, 1400-1401 (1938). (118) *Chem. Abstr.* 1938, 1400-1401 (1938). (119) *Chem. Abstr.* 1938, 1400-1401 (1938). (120) *Chem. Abstr.* 1938, 1400-1401 (1938). (121) *Chem. Abstr.* 1938, 1400-1401 (1938). (122) *Chem. Abstr.* 1938, 1400-1401 (1938). (123) *Chem. Abstr.* 1938, 1400-1401 (1938). (124) *Chem. Abstr.* 1938, 1400-1401 (1938). (125) *Chem. Abstr.* 1938, 1400-1401 (1938). (126) *Chem. Abstr.* 1938, 1400-1401 (1938). (127) *Chem. Abstr.* 1938, 1400-1401 (1938). (128) *Chem. Abstr.* 1938, 1400-1401 (1938). (129) *Chem. Abstr.* 1938, 1400-1401 (1938). (130) *Chem. Abstr.* 1938, 1400-1401 (1938). (131) *Chem. Abstr.* 1938, 1400-1401 (1938). (132) *Chem. Abstr.* 1938, 1400-1401 (1938). (133) *Chem. Abstr.* 1938, 1400-1401 (1938). (134) *Chem. Abstr.* 1938, 1400-1401 (1938). (135) *Chem. Abstr.* 1938, 1400-1401 (1938). (136) *Chem. Abstr.* 1938, 1400-1401 (1938). (137) *Chem. Abstr.* 1938, 1400-1401 (1938). (138) *Chem. Abstr.* 1938, 1400-1401 (1938). (139) *Chem. Abstr.* 1938, 1400-1401 (1938). (140) *Chem. Abstr.* 1938, 1400-1401 (1938). (141) *Chem. Abstr.* 1938, 1400-1401 (1938). (142) *Chem. Abstr.* 1938, 1400-1401 (1938). (143) *Chem. Abstr.* 1938, 1400-1401 (1938). (144) *Chem. Abstr.* 1938, 1400-1401 (1938). (145) *Chem. Abstr.* 1938, 1400-1401 (1938). (146) *Chem. Abstr.* 1938, 1400-1401 (1938). (147) *Chem. Abstr.* 1938, 1400-1401 (1938). (148) *Chem. Abstr.* 1938, 1400-1401 (1938). (149) *Chem. Abstr.* 1938, 1400-1401 (1938). (150) *Chem. Abstr.* 1938, 1400-1401 (1938).

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3:0985 18-CHLORO-OCTADECANOL-1  $C_{18}H_{37}OCl$  Beil. S.N. 24  
 ( $\omega$ -Chloro-n-octadecyl alcohol;  $\omega$ -chlorostearyl alcohol)  
 $CH_2(CH_2)_{16}CH_2OH$   
 $Cl$   
 M.P. 53-54.5° (1)


Colorless crystals.

[For prepn. from  $\alpha,\omega$ -octadecamethylene glycol (m.p. 97-98°) with  $SOCl_2$  + dimethylaniline in  $C_6H_6$  (50% yield) see (1); note that a little 1,18-dichlorooctadecano with m.p. 51° (i.e., practically the same as  $\bar{C}$ ) is also formed.]

$\bar{C}$  is only slightly attacked by  $KOH$  (2).

① 18-Chlorooctadecyl N-phenylcarbamate: Mts. from alc. or lt. pct., m.p. 77° (1).

3:0985 (1) Bennett, Gudgeon, *J. Chem. Soc.* 1938, 1679-1681. (2) Seck, Dittmar, *Chem. Umschau Fette, Öle, Wachse, Harze* 39, 226-229 (1932); *Cent.* 1933, I 1757, [*C.A.* 27, 703 (1933)].

3:0990 1,2,3-TRICHLOROBENZENE  $C_6H_3Cl_3$  Beil. V - 203  
 (trichlorobenzene)  
  
 $V_1$ -(112)  
 $V_2$ -(150)

M.P. 51° (1) B.P. 218-219° (3)  
 53-54° (2) (3)  
 52.5-53.0° (4)  
 52.4° (5)  
 52° (6)  
 50.8° (7)

Tbls. from alc.; cas. sol.  $CS_2$  or  $C_6H_6$ ; spar. sol. alc.; volatile with steam. [For use as component of mixtures for dif. inflammable electric insulating materials see (8).] [For thermal anal. of mixts. of  $\bar{C}$  with 1,2,4-trichlorobenzene (3,6420) and with 1,3,5-trichlorobenzene (3:1400) see (5).]

[For prepn. of  $\bar{C}$  from 2,3,4-trichloroaniline (Beil. XII-626) with ethyl nitrite (3) or by diazotization and reaction with alc. (35% yield (1)), or from 3,4,5-trichloroaniline (Beil.



## II. INDEX OF EMPIRICAL FORMULAS ACCORDING TO PERCENTAGE CHLORINE CONTENT

The empirical formulas for all groups of isomers listed in this book are represented below in diminishing order of their percentage chlorine. Note that there are numerous instances in which this value is the same for several different formulas. An analogous list of empirical formulas arranged according to their molecular weights comprises Index III (page 1383).

To ascertain which specific compounds corresponding to a given formula are described in the text of this volume, see the Empirical Formula Index (page 1359).

% Chlorine	Formula	% Chlorine	Formula	% Chlorine	Formula
92.2	$\text{CCl}_4$	76.9	$\text{C}_7\text{OCl}_4$	68.0	$\text{C}_7\text{OCl}_4$
89.9	$\text{C}_2\text{Cl}_6$	75.8	$\text{C}_2\text{O}_2\text{Cl}_6$	67.6	$\text{C}_4\text{H}_2\text{Cl}_2$
89.1	$\text{CHCl}_3$	74.7	$\text{C}_2\text{Cl}_2$	67.6	$\text{C}_6\text{H}_4\text{Cl}_4$
88.7	$\text{C}_3\text{Cl}_8$	74.7	$\text{C}_6\text{Cl}_4$	67.2	$\text{C}_6\text{O}_2\text{Cl}_4$
87.6	$\text{C}_2\text{HCl}_4$	74.5	$\text{C}_7\text{HCl}_7$	67.1	$\text{C}_7\text{H}_4\text{Cl}_4$
87.0	$\text{C}_2\text{HCl}_7$	73.9	$\text{C}_4\text{H}_2\text{Cl}_4$	66.9	$\text{C}_4\text{H}_2\text{O}_2\text{Cl}_4$
85.5	$\text{C}_2\text{Cl}_4$	73.2	$\text{C}_2\text{OCl}_4$	66.7	$\text{C}_4\text{H}_2\text{Cl}_2$
85.5	$\text{C}_3\text{Cl}_6$	73.1	$\text{C}_2\text{H}_2\text{Cl}_2$	66.6	$\text{C}_6\text{HOC}_2\text{Cl}_4$
85.0	$\text{C}_4\text{H}_2\text{Cl}_6$	73.1	$\text{C}_2\text{H}_2\text{Cl}_3$	65.9	$\text{C}_2\text{H}_2\text{OCl}_2$
84.8	$\text{C}_2\text{H}_2\text{Cl}_4$	73.1	$\text{C}_4\text{H}_4\text{Cl}_4$	65.9	$\text{C}_4\text{H}_7\text{Cl}_2$
84.7	$\text{C}_4\text{OCl}_{10}$	73.1	$\text{C}_6\text{H}_6\text{Cl}_4$	65.9	$\text{C}_4\text{H}_2\text{O}_2\text{Cl}_4$
84.5	$\text{C}_2\text{H}_2\text{Cl}_4$	72.5	$\text{C}_2\text{H}_2\text{Cl}_2$	65.7	$\text{C}_4\text{H}_2\text{Cl}_4$
83.5	$\text{CH}_2\text{Cl}_2$	72.4	$\text{C}_2\text{H}_2\text{OCl}_4$	65.1	$\text{C}_2\text{HO}_2\text{Cl}_2$
82.9	$\text{C}_4\text{H}_2\text{Cl}_7$	72.4	$\text{C}_4\text{H}_2\text{Cl}_4$	64.5	$\text{C}_2\text{H}_2\text{OCl}_2$
82.7	$\text{C}_2\text{HCl}_4$	72.2	$\text{C}_2\text{HOC}_2\text{Cl}_4$	64.5	$\text{C}_2\text{H}_2\text{Cl}_4$
82.5	$\text{C}_2\text{Cl}_2$	72.1	$\text{C}_2\text{H}_2\text{Cl}_2$	64.3	$\text{C}_2\text{H}_2\text{O}_2\text{Cl}_2$
82.0	$\text{C}_2\text{H}_2\text{Cl}_2$	72.0	$\text{C}_2\text{HO}_2\text{Cl}_2$	63.9	$\text{C}_2\text{H}_2\text{Cl}_2$
81.6	$\text{C}_4\text{Cl}_2$	71.7	$\text{COCl}_2$	63.9	$\text{C}_4\text{O}_2\text{Cl}_4$
81.1	$\text{C}_4\text{H}_2\text{OCl}_2$	71.7	$\text{C}_2\text{O}_2\text{Cl}_4$	63.7	$\text{C}_2\text{HOC}_2\text{Cl}_4$
81.0	$\text{C}_2\text{HCl}_2$	71.7	$\text{C}_2\text{H}_2\text{Cl}_2$	63.3	$\text{C}_2\text{H}_2\text{O}_2\text{Cl}_4$
81.0	$\text{C}_4\text{H}_2\text{Cl}_2$	71.7	$\text{C}_2\text{O}_2\text{Cl}_2$	63.3	$\text{C}_4\text{H}_{10}\text{Cl}_4$
80.3	$\text{C}_4\text{H}_4\text{Cl}_2$	71.7	$\text{C}_2\text{H}_2\text{OCl}_4$	62.8	$\text{C}_2\text{H}_2\text{OCl}_2$
79.7	$\text{C}_2\text{H}_2\text{Cl}_2$	71.2	$\text{C}_2\text{H}_2\text{OCl}_2$	62.8	$\text{C}_2\text{H}_2\text{Cl}_2$
78.8	$\text{C}_2\text{H}_2\text{Cl}_4$	71.2	$\text{C}_2\text{H}_2\text{Cl}_2$	62.8	$\text{C}_4\text{H}_2\text{O}_2\text{Cl}_4$
78.3	$\text{C}_4\text{HCl}_4$	70.8	$\text{C}_2\text{HCl}_2$	61.7	$\text{C}_2\text{H}_2\text{OCl}_2$
78.0	$\text{C}_2\text{OCl}_4$	70.7	$\text{C}_4\text{OCl}_2$	61.7	$\text{C}_2\text{H}_2\text{Cl}_4$
78.0	$\text{C}_2\text{H}_2\text{Cl}_4$	70.3	$\text{C}_{10}\text{Cl}_2$	61.3	$\text{C}_2\text{H}_2\text{Cl}_2$
77.6	$\text{C}_4\text{H}_2\text{Cl}_2$	70.2	$\text{CH}_2\text{Cl}_2$	61.2	$\text{C}_2\text{H}_2\text{OCl}_4$
77.0	$\text{C}_2\text{HOC}_2\text{Cl}_2$	68.9	$\text{C}_4\text{O}_2\text{Cl}_2$	60.6	$\text{C}_2\text{H}_2\text{O}_2\text{Cl}_2$
77.0	$\text{C}_4\text{H}_2\text{Cl}_2$	68.6	$\text{C}_4\text{H}_2\text{Cl}_2$	60.6	$\text{C}_4\text{H}_2\text{OCl}_2$

3,3'-Dichlorobenzophenone	3:3860	$C_{14}H_9OCl$	M.W. = 246.8	Cl = 14.4%
3,4-Dichlorobenzophenone	3:3979	Myristoyl chloride		3:9893
3,4'-Dichlorobenzophenone	3:3115			
3,5-Dichlorobenzophenone	3:1593	$C_{14}H_{13}OCl$	M.W. = 248.8	Cl = 14.2%
4,4'-Dichlorobenzophenone	3:4270	11-Chlorotetradecanol-1		3:0373
$C_{14}H_{11}OCl$	M.W. = 216.7	Cl = 16.4%	<b>C<sub>15</sub> GROUP</b>	
2-Chlorobenzophenone	3:0715	$C_{15}H_{25}OCl$	M.W. = 260.8	Cl = 13.6%
3-Chlorobenzophenone	3:2160	Pentadecanoyl chloride		3:9900
4-Chlorobenzophenone	3:1914			
$C_{15}H_{27}OCl$	M.W. = 232.8	Cl = 15.2%	<b>C<sub>16</sub> GROUP</b>	
Tridecanoyl chloride	3:9860	$C_{16}H_{33}OCl$	M.W. = 274.9	Cl = 12.9%
<b>C<sub>14</sub> GROUP</b>		Palmitoyl chloride		3:9912
$C_{14}H_{11}O_2Cl$	M.W. = 242.7	Cl = 14.6%	$C_{16}H_{25}OCl$	M.W. = 276.9
1-Chloroanthraquinone	3:4450		16-Chlorohexadecanol-1	3:0523
2-Chloroanthraquinone	3:4922			
$C_{14}H_{17}O_2Cl$	M.W. = 244.7	Cl = 14.5%	<b>C<sub>17</sub> GROUP</b>	
<i>o</i> -Benzoylbenzoyl chloride	3:9850	$C_{17}H_{29}OCl$	M.W. = 288.9	Cl = 12.3%
$C_{14}H_{15}OCl_2$	M.W. = 265.1	Cl = 20.8%	Heptadecanoyl chloride	3:9923
<i>o</i> -Chlorodiphenylacetyl chloride	3:9885		<b>C<sub>18</sub> GROUP</b>	
$C_{14}H_{17}O_2Cl_2$	M.W. = 281.1	Cl = 25.2%	$C_{18}H_{37}OCl$	M.W. = 300.9
<i>D</i> -( <i>p</i> -chlorophenyl)acetic acid	3:4612		Elaidyl chloride	3:0950
$C_{14}H_{19}OCl$	M.W. = 230.7	Cl = 15.4%	Oleoyl chloride	3:9940
<i>p</i> -Phenylphenacyl chloride	3:3334		$C_{18}H_{35}OCl$	M.W. = 302.9
Decyl chloride	3:1618		Stearoyl chloride	3:9960
$C_{14}H_{19}O_2Cl$	M.W. = 246.7	Cl = 14.4%	$C_{18}H_{33}OCl$	M.W. = 304.9
Diphenylchloroacetic acid	3:3353		18-Chlorooctadecanol-1	3:0983

% Chlorine	Formula	% Chlorine	Formula	% Chlorine	Formula
28.7	$C_{14}H_8Cl_2$	22.6	$C_8H_9OCl$	17.7	$C_{15}H_{11}O_2Cl$
28.5	$C_4H_9O_2Cl$	22.4	$C_9H_{10}Cl$	17.5	$C_{12}H_{11}Cl$
28.5	$C_{14}H_{10}Cl_2$	22.1	$C_9H_{17}Cl$	17.3	$C_{11}H_{12}OCl$
28.3	$C_{14}H_{13}Cl_2$	21.8	$C_7H_{11}O_2Cl$	17.3	$C_{12}H_9OCl$
28.2	$C_{13}H_9OC_2Cl_2$	21.8	$C_8H_{15}OCl$	17.3	$C_{12}H_{13}Cl$
28.0	$C_7H_7Cl$	21.8	$C_9H_9Cl$	17.2	$C_8H_{11}O_4Cl$
27.6	$C_8H_9OCl$	21.8	$C_{10}H_7Cl$	17.2	$C_{11}H_7O_2Cl$
27.6	$C_7H_9Cl$	21.5	$C_8H_9O_2Cl$	16.4	$C_{13}H_9OCl$
27.2	$C_9H_9O_2Cl$	21.5	$C_7H_{13}O_2Cl$	16.2	$C_{12}H_{23}OCl$
27.1	$C_7H_{11}Cl$	21.5	$C_8H_{17}OCl$	16.2	$C_{13}H_{17}Cl$
26.8	$C_4HO_3Cl$	21.5	$C_9H_9OCl$	16.1	$C_{12}H_{13}OCl$
26.8	$C_{11}H_{10}OCl_2$	21.3	$C_9H_{11}O_2Cl$	15.6	$C_9H_{10}O_4Cl$
26.7	$C_8H_9OCl$	21.3	$C_8H_7OCl$	15.4	$C_{14}H_{11}OCl$
26.7	$C_7H_{13}Cl$	21.0	$C_8H_9OCl$	15.2	$C_{13}H_{13}OCl$
26.4	$C_8H_7O_2Cl$	21.0	$C_{10}H_{13}Cl$	15.2	$C_{14}H_{29}Cl$
26.3	$C_8H_{11}OCl$	20.8	$C_8H_7O_2Cl$	15.1	$C_{11}H_{19}O_2Cl$
26.3	$C_7H_{17}Cl$	20.8	$C_8H_{11}OCl$	14.6	$C_{14}H_7O_2Cl$
26.0	$C_8H_9O_2Cl$	20.6	$C_7H_9O_2Cl$	14.5	$C_{14}H_9O_2Cl$
26.0	$C_9H_9O_2Cl$	20.5	$C_{10}H_{17}Cl$	14.4	$C_9H_9O_4Cl$
26.0	$C_8H_{11}OCl$	20.3	$C_{10}H_{19}Cl$	14.4	$C_{14}H_{11}O_2Cl$
25.6	$C_8H_7O_2Cl$	20.1	$C_9H_{17}OCl$	14.4	$C_{14}H_{17}OCl$
25.6	$C_8H_7Cl$	20.1	$C_{10}H_{19}Cl$	14.4	$C_{13}H_{21}Cl$
25.2	$C_7H_9OCl$	20.1	$C_{11}H_7Cl$	14.2	$C_{14}H_{29}OCl$
25.2	$C_8H_9Cl$	19.9	$C_8H_7O_2Cl$	13.6	$C_{13}H_{19}OCl$
25.2	$C_{11}H_{10}O_2Cl_2$	19.9	$C_9H_{13}O_2Cl$	13.5	$C_{14}H_{25}Cl$
25.1	$C_8H_9Cl$	19.8	$C_9H_{13}OCl$	12.9	$C_{12}H_{25}OCl$
24.9	$C_9H_9O_2Cl$	19.8	$C_{10}H_7OCl$	12.9	$C_{17}H_{19}Cl$
24.9	$C_7H_7OCl$	19.6	$C_8H_{17}O_2Cl$	12.8	$C_{19}H_{23}OCl$
24.5	$C_9H_9O_2Cl$	19.6	$C_9H_9O_2Cl$	12.7	$C_{10}H_{13}Cl$
24.5	$C_8H_{13}Cl$	19.4	$C_8H_{11}O_2Cl$	12.3	$C_{17}H_{33}OCl$
24.2	$C_7H_{11}OCl$	19.4	$C_9H_9O_2Cl$	12.3	$C_{13}H_{17}Cl$
24.2	$C_8H_{19}Cl$	19.4	$C_{10}H_{11}OCl$	12.2	$C_{10}H_{19}Cl$
23.9	$C_9H_9O_2Cl$	19.2	$C_8H_9O_2Cl$	11.8	$C_{13}H_{25}OCl$
23.9	$C_7H_{13}OCl$	19.2	$C_9H_7O_2Cl$	11.7	$C_{13}H_{35}OCl$
23.9	$C_8H_{17}Cl$	19.2	$C_{10}H_{19}OCl$	11.7	$C_{14}H_{19}Cl$
23.6	$C_8H_9O_2Cl$	19.0	$C_9H_7O_2Cl$	11.6	$C_{12}H_{17}OCl$
23.5	$C_8H_7O_2Cl$	18.8	$C_{12}H_7Cl$		
23.5	$C_9H_{11}O_2Cl$	18.6	$C_{10}H_{19}OCl$		
23.5	$C_7H_{13}OCl$	18.6	$C_{11}H_{27}Cl$		
23.2	$C_9H_9O_2Cl$	18.6	$C_{11}H_7OCl$		
23.2	$C_9H_{13}O_2Cl$	18.5	$C_{10}H_4O_2Cl_2$		
23.2	$C_9H_9Cl$	18.4	$C_{10}H_7O_2Cl$		
22.9	$C_9H_7OCl$	18.4	$C_{10}H_{21}OCl$		
22.9	$C_8H_{11}Cl$	18.2	$C_7H_{11}O_2Cl$		
22.7	$C_7H_9O_2Cl$	17.7	$C_8H_9O_4Cl$		

% Chlorine	Formula	% Chlorine	Formula	% Chlorine	Formula
60.6	$C_6H_5Cl_2$	48.0	$C_6H_7O_2Cl_2$	38.3	$C_4H_5Cl$
60.2	$C_7H_5O_2Cl_2$	48.0	$C_6H_{11}O_2Cl_2$	37.9	$C_4H_4O_2Cl_2$
59.9	$C_4H_7OCl_2$	47.6	$C_7H_7Cl$	37.9	$C_5H_6O_2Cl_2$
59.6	$C_4Cl_2$	47.6	$C_6H_4Cl_2$	37.9	$C_5H_{11}O_2Cl_2$
59.2	$C_4H_3O_2Cl_4$	47.6	$C_2H_4OCl_2$	37.5	$C_2H_3O_2Cl$
58.6	$C_2HCl$	47.2	$C_7H_5O_2Cl_2$	37.5	$C_3H_7OCl$
58.6	$C_4H_2Cl_2$	47.2	$C_6H_7OCl_2$	37.5	$C_5H_5OCl_2$
58.1	$C_3OCl_2$	47.0	$C_6H_5Cl_2$	37.5	$C_{14}H_3Cl_2$
58.1	$C_7H_7OCl_2$	46.7	$C_6H_2O_2Cl_2$	37.2	$C_{14}H_{11}Cl_2$
58.0	$C_5H_3Cl_2$	46.4	$C_4H_2O_2Cl_2$	37.1	$C_7H_4O_2Cl_2$
57.7	$C_4H_2Cl_2$	46.4	$C_6H_5O_2Cl_2$	37.1	$C_3H_5OCl_2$
57.7	$C_3O_2Cl_4$	46.3	$C_2H_2Cl$	36.0	$C_7H_{10}O_2Cl_2$
57.4	$C_5H_7Cl_2$	46.3	$C_6H_{11}Cl_2$	36.0	$C_2H_{11}Cl_2$
57.2	$C_5H_3O_2Cl_4$	46.0	$C_{10}H_4Cl_2$	36.0	$C_{13}H_4Cl_2$
56.8	$C_4HO_2Cl_2$	45.7	$C_4H_4O_2Cl_2$	34.9	$C_3H_4O_2Cl_2$
56.7	$C_2H_2Cl$	45.7	$C_6H_5OCl_2$	34.6	$C_6H_7Cl$
56.7	$C_4H_6Cl_2$	45.7	$C_6H_{12}Cl_2$	34.3	$C_7H_4O_2Cl_2$
56.7	$C_6H_5Cl_2$	45.6	$C_7H_{11}O_2Cl_2$	33.0	$C_6HO_2Cl$
56.0	$C_3H_3O_2Cl_2$	45.2	$C_2H_4OCl$	33.0	$C_4H_7OCl$
55.0	$C_2O_2Cl_2$	45.2	$C_4H_4O_2Cl_2$	33.0	$C_6H_4Cl$
55.9	$C_4H_4OCl_2$	45.2	$C_6H_4O_2Cl_2$	33.9	$C_3H_2O_2Cl_2$
55.8	$C_4H_4Cl_2$	45.1	$C_5H_7Cl$	33.6	$C_9H_{12}O_2Cl_2$
55.6	$C_4H_4O_2Cl_2$	44.6	$C_6H_5O_2Cl_2$	33.6	$C_{10}H_{20}Cl_2$
55.1	$C_2H_2Cl$	44.6	$C_{14}H_4Cl_2$	33.3	$C_4H_3O_2Cl$
55.0	$C_2H_2O_2Cl_2$	44.3	$C_{11}H_{16}Cl_2$	33.3	$C_6H_7OCl$
55.0	$C_2H_3OCl_2$	44.0	$C_2H_6OCl$	33.3	$C_4H_{11}Cl$
55.0	$C_4H_7O_2Cl_2$	44.0	$C_2H_4Cl_2$	33.3	$C_{10}H_4OCl_2$
54.7	$C_{14}H_4Cl_2$	43.5	$C_6H_4OCl_2$	33.3	$C_{11}H_{10}O_2Cl_2$
54.6	$C_7H_{12}O_2Cl_4$	42.5	$C_6O_2Cl_2$	33.0	$C_4H_3O_2Cl_2$
54.4	$C_7H_3Cl_2$	42.0	$C_4H_4O_2Cl_2$	33.0	$C_7H_{12}O_2Cl_2$
54.2	$C_2H_4O_2Cl_2$	41.0	$C_7H_{11}Cl_2$	32.7	$C_2H_4O_2Cl$
53.0	$C_6H_2OCl_2$	41.6	$C_6H_{10}OCl_2$	32.7	$C_4H_7OCl$
52.5	$C_{10}H_{11}Cl_4$	41.6	$C_6H_5O_2Cl_2$	32.7	$C_3H_2O_2Cl_2$
51.8	$C_3H_3Cl_2$	41.5	$C_4H_4O_2Cl_2$	32.1	$C_3H_7O_2Cl$
51.8	$C_3H_7O_2Cl_2$	41.5	$C_4H_4O_2Cl_2$	32.1	$C_3H_2O_2Cl_2$
51.3	$C_4H_5O_2Cl_2$	41.0	$C_4H_2Cl$	31.8	$C_{11}H_{11}Cl_2$
51.0	$C_3H_2Cl_2$	41.0	$C_4H_5O_2Cl_2$	31.5	$C_4H_2Cl$
50.8	$C_7H_7OCl_2$	40.5	$C_7H_4OCl_2$	31.5	$C_3H_{11}O_2Cl_2$
50.3	$C_4H_2O_2Cl_2$	40.5	$C_3H_4Cl_2$	30.4	$C_4H_2Cl$
50.3	$C_4H_4OCl_2$	40.1	$C_4H_4Cl$	30.2	$C_3H_4O_2Cl_2$
50.3	$C_6H_{12}Cl_2$	40.1	$C_6H_3O_2Cl_2$	29.9	$C_3H_7OCl$
50.3	$C_7H_{10}O_2Cl_4$	40.1	$C_7H_7OCl_2$	29.0	$C_4H_{11}Cl$
50.3	$C_7H_4OCl_2$	39.8	$C_4H_4O_2Cl_2$	29.0	$C_{11}H_{16}Cl_2$
50.0	$C_{11}H_4Cl_2$	39.0	$C_7H_{12}Cl_2$	29.7	$C_{13}H_{11}O_2Cl_2$
49.8	$C_4H_3O_2Cl_2$	39.2	$C_4H_3OCl$	29.6	$C_4H_{10}O_2Cl_2$
49.6	$C_3H_2O_2Cl_2$	39.2	$C_4H_2Cl$	29.4	$C_4H_2O_2Cl$
49.6	$C_4H_4OCl_2$	38.7	$C_6H_5O_2Cl_2$	29.4	$C_4H_2OCl$
49.6	$C_4O_2Cl_4$	38.7	$C_7H_{10}Cl_2$	29.4	$C_4H_{11}Cl$
48.6	$C_4H_5O_2Cl_2$	38.3	$C_7H_7OCl$	28.0	$C_4H_2O_2Cl$
48.2	$C_4H_4Cl_2$	38.3	$C_4H_2O_2Cl_2$	28.0	$C_4H_{11}OCl$

M.W.	Formula	M.W.	Formula	M.W.	Formula
152.6	$C_6H_5O_2Cl$	173.0	$C_6H_5O_2Cl_2$	191.1	$C_8H_5OCl_4$
152.6	$C_6H_{13}O_2Cl$	173.5	$C_6H_7Cl_2$	191.5	$C_8H_5O_2Cl_3$
152.6	$C_6H_9Cl$	174.7	$C_{10}H_{11}Cl$	191.6	$C_{10}H_4O_2Cl_2$
153.0	$C_6H_2O_2Cl_2$	175.0	$C_7H_4OCl_4$	191.9	$C_8H_7Cl_4$
153.1	$C_6H_{10}Cl_2$	175.1	$C_8H_9Cl_2$	192.6	$C_{10}H_1O_2Cl$
153.8	$CCl_4$	175.4	$C_9H_2O_2Cl_2$	192.6	$C_{10}H_{21}OCl$
154.6	$C_6H_7OCl$	175.5	$C_9H_5OCl_3$	193.6	$C_8H_7O_2Cl_3$
154.6	$C_6H_{11}Cl$	175.5	$C_8H_9Cl_3$	193.9	$C_7OCl_4$
155.0	$C_6H_4O_2Cl_2$	176.6	$C_{11}H_9Cl$	193.9	$C_4H_4Cl_4$
155.0	$C_6H_5OCl_4$	176.7	$C_9H_{17}OCl$	194.6	$C_7H_{11}O_2Cl$
155.1	$C_6H_{12}Cl_2$	176.7	$C_{10}H_{11}Cl$	195.5	$C_7H_8Cl_3$
156.6	$C_7H_7O_2Cl$	177.0	$C_8H_2O_2Cl_4$	195.9	$C_8H_5OCl_4$
156.6	$C_8H_9OCl$	177.0	$C_7H_8OCl_2$	195.9	$C_8H_8Cl_4$
157.0	$C_6H_4O_3Cl_2$	177.4	$C_8H_5O_2Cl_3$	197.1	$C_8H_{10}O_2Cl_2$
157.4	$C_6H_2Cl_3$	177.5	$C_8H_7OCl_3$	197.1	$C_8H_{10}Cl_4$
158.7	$C_8H_{13}Cl$	178.6	$C_8H_7O_4Cl$	197.1	$C_{10}H_6Cl_4$
159.0	$C_8H_5O_2Cl_2$	178.6	$C_{10}H_7OCl$	197.5	$C_8H_9OCl_3$
159.5	$C_8H_9Cl_3$	178.7	$C_8H_{11}O_2Cl$	197.8	$C_2O_2Cl_4$
160.7	$C_8H_{17}Cl$	178.7	$C_9H_{13}OCl$	197.9	$C_8H_9OCl_4$
161.0	$C_7H_8Cl_2$	179.0	$C_8H_4O_2Cl_2$	200.6	$C_8H_4O_4Cl$
161.4	$C_8H_9OCl_3$	179.1	$C_8H_{12}Cl_2$	200.7	$C_{12}H_{13}O_2Cl$
161.5	$C_8H_7Cl_3$	179.9	$C_8H_2Cl_4$	202.3	$C_2HCl_3$
162.6	$C_7H_{11}O_2Cl$	180.6	$C_8H_5O_3Cl$	202.7	$C_{18}H_{11}Cl$
162.6	$C_{10}H_7Cl$	180.7	$C_8H_{17}O_2Cl$	203.0	$C_8H_9O_2Cl_3$
162.7	$C_8H_{15}OCl$	181.5	$C_8H_8Cl_3$	204.7	$C_{11}H_{21}OCl$
162.7	$C_9H_{13}Cl$	181.8	$C_2OCl_4$	204.7	$C_{13}H_4OCl$
163.0	$C_8H_4OCl_2$	181.9	$C_8H_4Cl_4$	204.8	$C_{12}H_{22}Cl$
163.4	$C_2HO_2Cl_3$	182.6	$C_8H_{11}O_4Cl$	205.5	$C_8H_7O_2Cl_3$
163.4	$C_8H_5OCl_3$	182.6	$C_8H_7O_3Cl$	206.6	$C_8H_{11}O_4Cl$
164.6	$C_8H_5O_2Cl$	182.6	$C_{10}H_{11}OCl$	206.6	$C_{11}H_7O_2Cl$
164.6	$C_7H_{13}O_2Cl$	183.0	$C_8H_5O_3Cl_2$	207.0	$C_7H_4O_3Cl_3$
164.6	$C_8H_9OCl$	183.1	$C_8H_{10}Cl_2$	207.5	$C_8H_5O_2Cl_3$
164.7	$C_8H_{17}OCl$	183.5	$C_8H_8Cl_3$	209.0	$C_8H_7O_4Cl_2$
165.4	$C_8H_5O_2Cl_2$	184.6	$C_8H_5O_3Cl$	209.5	$C_7H_8OCl_4$
165.8	$C_2Cl_4$	184.6	$C_8H_7O_2Cl$	209.9	$C_8H_8Cl_4$
166.6	$C_8H_7OCl$	184.7	$C_{10}H_{13}OCl$	211.1	$C_8H_{12}O_2Cl_2$
166.7	$C_7H_{13}O_2Cl$	185.0	$C_8H_2O_4Cl_2$	211.2	$C_{10}H_{20}Cl_2$
167.0	$C_4O_2Cl_2$	185.5	$C_8H_7Cl_4$	211.4	$C_8HO_2Cl_2$
167.9	$C_4H_2Cl_4$	186.6	$C_8H_7O_4Cl$	211.5	$C_7H_7OCl_3$
168.6	$C_8H_9OCl$	187.0	$C_8H_4O_4Cl_2$	211.9	$C_8H_5O_2Cl_4$
168.7	$C_{10}H_{13}Cl$	187.0	$C_8H_4O_5Cl_2$	213.1	$C_{12}H_6OCl_2$
169.0	$C_8H_5O_3Cl_2$	187.1	$C_8H_{17}O_2Cl_3$	213.5	$C_8H_7O_2Cl_3$
169.1	$C_7H_{14}Cl_2$	187.4	$C_8HO_2Cl_3$	214.3	$C_8HCl_6$
170.6	$C_8H_7O_2Cl$	187.5	$C_8H_7Cl_4$	216.0	$C_8H_5O_4Cl_2$
170.6	$C_8H_{11}OCl$	188.7	$C_{21}H_7Cl$	215.1	$C_7H_{17}O_2Cl_2$
171.0	$C_8H_4O_2Cl_2$	189.0	$C_8H_5OCl_2$	216.9	$C_8H_2Cl_4$
171.0	$C_8H_5O_2Cl_2$	190.5	$C_{12}H_7OCl$	216.3	$C_7H_5Cl_4$
171.1	$C_8H_{13}OCl_4$	190.7	$C_{10}H_{13}OCl$	216.7	$C_{12}H_7OCl$
172.6	$C_7H_8O_2Cl$	190.8	$C_{11}H_{12}Cl$	216.7	$C_7H_{12}Cl$
172.7	$C_{12}H_{17}Cl$	191.0	$C_7H_4O_2Cl_2$	217.0	$C_8H_5O_2Cl_3$

### III. INDEX OF EMPIRICAL FORMULAS ACCORDING TO MOLECULAR WEIGHTS

The empirical formulas for all groups of isomers listed in this book are represented below in increasing order of their molecular weights. Note that there are numerous instances in which this value is the same for several different formulas. An analogous list of empirical formulas arranged according to their percentage chlorine comprises Index II (page 1380).

To ascertain which specific compounds corresponding to a given formula are described in the text of this volume see the Empirical Formula Index (page 1359).

M.W.	Formula	M.W.	Formula	M.W.	Formula
50.5	$\text{C}_2\text{H}_5\text{Cl}$	113.0	$\text{C}_5\text{H}_9\text{Cl}_2$	136.5	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$
60.5	$\text{C}_3\text{H}_7\text{Cl}$	115.0	$\text{C}_5\text{H}_9\text{OCl}_2$	136.6	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$
62.5	$\text{C}_3\text{H}_7\text{Cl}$	116.0	$\text{C}_5\text{H}_7\text{Cl}$	136.0	$\text{C}_6\text{H}_{11}\text{OCl}$
64.5	$\text{C}_3\text{H}_7\text{Cl}$	118.6	$\text{C}_5\text{H}_7\text{OCl}$	136.6	$\text{C}_6\text{H}_7\text{Cl}$
74.5	$\text{C}_4\text{H}_9\text{Cl}$	118.6	$\text{C}_5\text{H}_{11}\text{Cl}$	137.0	$\text{C}_6\text{H}_9\text{Cl}_2$
76.5	$\text{C}_4\text{H}_9\text{Cl}$	119.0	$\text{C}_6\text{Cl}_2$	138.6	$\text{C}_6\text{H}_7\text{O}_2\text{Cl}$
78.5	$\text{C}_4\text{H}_9\text{OCl}$	119.4	$\text{C}_6\text{HCl}_2$	138.6	$\text{C}_6\text{H}_7\text{Cl}$
78.5	$\text{C}_4\text{H}_7\text{Cl}$	120.5	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$	139.0	$\text{C}_6\text{H}_9\text{Cl}_2$
80.5	$\text{C}_4\text{H}_9\text{OCl}$	120.6	$\text{C}_6\text{H}_7\text{OCl}$	140.0	$\text{C}_7\text{H}_7\text{OCl}$
84.9	$\text{C}_4\text{H}_7\text{Cl}_2$	120.6	$\text{C}_6\text{H}_{11}\text{Cl}$	140.6	$\text{C}_6\text{H}_9\text{Cl}$
86.5	$\text{C}_4\text{H}_7\text{Cl}$	122.6	$\text{C}_6\text{H}_7\text{O}_2\text{Cl}$	141.0	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}_2$
88.5	$\text{C}_4\text{H}_9\text{Cl}$	122.6	$\text{C}_6\text{H}_{11}\text{OCl}$	141.0	$\text{C}_6\text{H}_9\text{OCl}_2$
90.5	$\text{C}_4\text{H}_7\text{OCl}$	123.0	$\text{C}_6\text{H}_9\text{Cl}_2$	141.0	$\text{C}_6\text{H}_{11}\text{Cl}_2$
90.6	$\text{C}_4\text{H}_7\text{Cl}$	124.1	$\text{C}_6\text{OCl}_2$	142.5	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$
92.5	$\text{C}_4\text{H}_7\text{OCl}$	124.0	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$	142.6	$\text{C}_7\text{H}_7\text{OCl}$
92.6	$\text{C}_4\text{H}_7\text{Cl}$	125.0	$\text{C}_6\text{H}_7\text{Cl}_2$	143.0	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}_2$
94.5	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$	126.6	$\text{C}_6\text{H}_7\text{Cl}$	143.0	$\text{C}_6\text{H}_9\text{OCl}_2$
94.5	$\text{C}_6\text{H}_7\text{OCl}$	126.9	$\text{C}_6\text{O}_2\text{Cl}_2$	144.6	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$
94.0	$\text{C}_5\text{Cl}_3$	127.0	$\text{C}_6\text{H}_7\text{OCl}_2$	144.6	$\text{C}_6\text{H}_{11}\text{Cl}$
97.0	$\text{C}_5\text{H}_9\text{Cl}_2$	127.0	$\text{C}_6\text{H}_9\text{Cl}_2$	145.4	$\text{C}_7\text{H}_7\text{Cl}_2$
98.0	$\text{COCl}_2$	128.6	$\text{C}_6\text{H}_9\text{OCl}$	146.6	$\text{C}_7\text{H}_{11}\text{OCl}$
99.0	$\text{C}_6\text{H}_9\text{Cl}_2$	128.6	$\text{C}_6\text{H}_7\text{Cl}$	146.7	$\text{C}_6\text{H}_{11}\text{Cl}$
102.6	$\text{C}_6\text{H}_7\text{Cl}$	128.9	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}_2$	147.0	$\text{C}_6\text{H}_9\text{Cl}_2$
104.5	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$	129.0	$\text{C}_6\text{H}_7\text{OCl}_2$	147.4	$\text{C}_6\text{H}_9\text{OCl}_2$
104.5	$\text{C}_6\text{H}_7\text{OCl}$	130.5	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$	147.4	$\text{C}_6\text{H}_9\text{Cl}_2$
104.6	$\text{C}_6\text{H}_7\text{Cl}$	130.6	$\text{C}_6\text{H}_{11}\text{Cl}$	148.0	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$
106.5	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$	131.0	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}_2$	148.6	$\text{C}_7\text{H}_{11}\text{OCl}$
106.6	$\text{C}_6\text{H}_7\text{OCl}_2$	131.4	$\text{C}_6\text{HCl}_3$	148.7	$\text{C}_6\text{H}_{11}\text{Cl}$
106.6	$\text{C}_6\text{H}_{11}\text{Cl}$	132.5	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$	149.0	$\text{C}_6\text{H}_9\text{Cl}_2$
108.5	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$	132.6	$\text{C}_6\text{H}_7\text{OCl}$	149.4	$\text{C}_6\text{H}_9\text{OCl}_2$
108.6	$\text{C}_6\text{H}_7\text{OCl}$	132.6	$\text{C}_6\text{H}_{11}\text{Cl}$	150.5	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$
110.5	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$	133.4	$\text{C}_6\text{H}_7\text{Cl}_2$	150.6	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$
111.0	$\text{C}_6\text{H}_7\text{Cl}_2$	134.6	$\text{C}_6\text{H}_9\text{O}_2\text{Cl}$	150.6	$\text{C}_6\text{H}_{11}\text{O}_2\text{Cl}$
112.6	$\text{C}_6\text{H}_9\text{Cl}$	134.6	$\text{C}_6\text{H}_{11}\text{OCl}$	150.7	$\text{C}_7\text{H}_{11}\text{OCl}$
112.9	$\text{C}_6\text{H}_7\text{OCl}_2$	134.7	$\text{C}_6\text{H}_{11}\text{Cl}$	151.0	$\text{C}_6\text{H}_7\text{Cl}_2$

#### IV. INDEX OF COMPOUNDS ACCORDING TO CHEMICAL TYPES

The numerous individual compounds of Order III whose preparation, properties, and reactions comprise the main text of this book are there listed in progressively increasing order of melting points (Division A, Solids), boiling points (Division B, Liquids), or empirical formulas (Division C, liquids for which data at ordinary pressure are not available). Unlike the treatment of Order I in an earlier volume, the compounds of the present Order III are not subdivided into genera. For this reason a highly useful feature of this volume is the following Chemical Type Index in which each compound is listed in one (or more) of the following eight arbitrary units.

- |  |  |
|--|--|
| UNIT 1. Chloro substitution products of saturated acyclic hydrocarbons.  | UNIT 5. Chlorosubstitution products (and their relatives) of carbonyl compounds. |
| UNIT 2. Chloro substitution products of unsaturated acyclic hydrocarbons | UNIT 6. Chloro substitution products of carboxylic acids and anhydrides.         |
| UNIT 3. Chloro substitution products of cyclic hydrocarbons.             | UNIT 7. Acyl chlorides.  |
| UNIT 4. Chloro substitution products of hydroxy compounds.               | UNIT 8. Chlorine substitution products of ethers and of esters.                  |

In order to facilitate recognition of the extent of subdivision of the above eight *units*, a brief summary of the subclassification is placed at the head of each one. Note that the names employed in this index are those best suited to recognition of the chemical relationships involved, and are not necessarily the same as those selected as principal names in the individual descriptions in the text.

Attention is also called to the fact that, in addition to this chemical type index, this volume is provided with conventional alphabetical name index and with empirical formula index.

##### UNIT 1. CHLORO SUBSTITUTION PRODUCTS OF ACYCLIC SATURATED HYDROCARBONS

*(Summary of Classification of Unit 1)*

###### A. MONOCHLORO DERIVATIVES.

1. With primary halogen.
2. With secondary halogen.
3. With tertiary halogen.

M.W.	Formula	M.W.	Formula	M.W.	Formula
218.8	C <sub>12</sub> H <sub>22</sub> OCl	244.4	C <sub>8</sub> H <sub>7</sub> Cl <sub>5</sub>	285.6	C <sub>14</sub> H <sub>11</sub> Cl <sub>3</sub>
218.8	C <sub>12</sub> H <sub>27</sub> Cl	244.6	C <sub>8</sub> H <sub>5</sub> O <sub>2</sub> Cl	285.9	C <sub>8</sub> O <sub>3</sub> Cl <sub>4</sub>
219.5	C <sub>8</sub> H <sub>5</sub> O <sub>2</sub> Cl <sub>2</sub>	244.7	C <sub>14</sub> H <sub>20</sub> O <sub>2</sub> Cl	288.9	C <sub>17</sub> H <sub>23</sub> OCl
219.9	C <sub>8</sub> H <sub>5</sub> Cl <sub>4</sub>	245.9	C <sub>9</sub> O <sub>2</sub> Cl <sub>4</sub>	288.9	C <sub>15</sub> H <sub>17</sub> Cl
220.8	C <sub>12</sub> H <sub>25</sub> OCl	246.3	C <sub>8</sub> HO <sub>2</sub> Cl <sub>5</sub>	290.8	C <sub>8</sub> H <sub>5</sub> Cl <sub>4</sub>
221.0	C <sub>8</sub> H <sub>5</sub> O <sub>2</sub> Cl <sub>2</sub>	246.7	C <sub>14</sub> H <sub>15</sub> O <sub>2</sub> Cl	290.8	C <sub>20</sub> H <sub>10</sub> Cl
221.5	C <sub>8</sub> H <sub>7</sub> O <sub>2</sub> Cl <sub>3</sub>	246.8	C <sub>14</sub> H <sub>27</sub> OCl	294.4	C <sub>7</sub> H <sub>3</sub> O <sub>2</sub> Cl <sub>5</sub>
221.5	C <sub>8</sub> H <sub>11</sub> O <sub>2</sub> Cl <sub>4</sub>	246.9	C <sub>15</sub> H <sub>11</sub> Cl	296.8	C <sub>3</sub> O <sub>3</sub> Cl <sub>5</sub>
221.9	C <sub>4</sub> O <sub>2</sub> Cl <sub>4</sub>	247.1	C <sub>14</sub> H <sub>3</sub> Cl <sub>2</sub>	298.8	C <sub>7</sub> H <sub>2</sub> Cl <sub>5</sub>
223.1	C <sub>12</sub> H <sub>9</sub> Cl <sub>2</sub>	247.9	C <sub>8</sub> H <sub>5</sub> O <sub>2</sub> Cl <sub>4</sub>	299.3	C <sub>8</sub> H <sub>3</sub> Cl <sub>7</sub>
223.5	C <sub>8</sub> H <sub>5</sub> OCl <sub>3</sub>	248.8	C <sub>2</sub> Cl <sub>4</sub>	300.8	C <sub>7</sub> OCl <sub>5</sub>
223.9	C <sub>4</sub> H <sub>2</sub> O <sub>2</sub> Cl <sub>4</sub>	248.8	C <sub>14</sub> H <sub>29</sub> OCl	300.9	C <sub>14</sub> H <sub>23</sub> OCl
224.0	C <sub>8</sub> H <sub>10</sub> Cl <sub>4</sub>	249.1	C <sub>15</sub> H <sub>10</sub> Cl <sub>2</sub>	302.9	C <sub>14</sub> H <sub>23</sub> OCl
225.1	C <sub>8</sub> H <sub>14</sub> O <sub>2</sub> Cl <sub>2</sub>	250.4	C <sub>8</sub> HCl <sub>4</sub>	303.9	C <sub>8</sub> H <sub>2</sub> O <sub>4</sub> Cl <sub>4</sub>
225.4	C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> Cl <sub>3</sub>	250.8	C <sub>8</sub> H <sub>2</sub> Cl <sub>4</sub>	304.9	C <sub>18</sub> H <sub>17</sub> OCl
225.5	C <sub>8</sub> H <sub>7</sub> OCl <sub>3</sub>	251.1	C <sub>15</sub> H <sub>3</sub> OCl <sub>2</sub>	308.8	C <sub>4</sub> O <sub>3</sub> Cl <sub>4</sub>
225.9	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub> Cl <sub>4</sub>	251.2	C <sub>14</sub> H <sub>12</sub> Cl <sub>2</sub>	312.8	C <sub>7</sub> OCl <sub>6</sub>
226.3	C <sub>4</sub> HCl <sub>4</sub>	255.5	C <sub>8</sub> H <sub>5</sub> O <sub>2</sub> Cl <sub>3</sub>	316.8	C <sub>8</sub> O <sub>2</sub> Cl <sub>5</sub>
226.7	C <sub>8</sub> H <sub>15</sub> O <sub>5</sub> Cl	258.4	C <sub>8</sub> H <sub>9</sub> Cl <sub>5</sub>	318.0	C <sub>16</sub> H <sub>5</sub> Cl <sub>4</sub>
228.4	C <sub>8</sub> H <sub>3</sub> Cl <sub>4</sub>	259.9	C <sub>7</sub> H <sub>4</sub> O <sub>2</sub> Cl <sub>4</sub>	319.7	C <sub>8</sub> Cl <sub>5</sub>
229.5	C <sub>8</sub> H <sub>3</sub> O <sub>2</sub> Cl <sub>3</sub>	260.8	C <sub>4</sub> Cl <sub>4</sub>	319.7	C <sub>15</sub> H <sub>21</sub> O <sub>2</sub> Cl <sub>2</sub>
230.0	C <sub>7</sub> H <sub>4</sub> Cl <sub>4</sub>	260.8	C <sub>16</sub> H <sub>25</sub> OCl	320.1	C <sub>14</sub> H <sub>10</sub> Cl <sub>4</sub>
230.3	C <sub>8</sub> HOCl <sub>4</sub>	260.9	C <sub>14</sub> H <sub>23</sub> Cl	322.8	C <sub>8</sub> H <sub>5</sub> O <sub>2</sub> Cl <sub>6</sub>
230.4	C <sub>4</sub> H <sub>2</sub> Cl <sub>4</sub>	262.8	C <sub>8</sub> H <sub>2</sub> Cl <sub>5</sub>	333.3	C <sub>7</sub> HCl <sub>7</sub>
230.7	C <sub>14</sub> H <sub>11</sub> OCl	264.4	C <sub>7</sub> H <sub>2</sub> Cl <sub>4</sub>	333.8	C <sub>4</sub> H <sub>2</sub> Cl <sub>5</sub>
231.5	C <sub>10</sub> H <sub>1</sub> Cl <sub>2</sub>	264.8	C <sub>4</sub> H <sub>4</sub> Cl <sub>5</sub>	343.7	C <sub>8</sub> Cl <sub>5</sub>
231.0	C <sub>8</sub> H <sub>2</sub> OCl <sub>4</sub>	265.1	C <sub>15</sub> H <sub>10</sub> OCl <sub>3</sub>	349.8	C <sub>4</sub> H <sub>3</sub> OCl <sub>4</sub>
232.8	C <sub>12</sub> H <sub>17</sub> OCl	266.4	C <sub>8</sub> HOCl <sub>3</sub>	354.5	C <sub>14</sub> H <sub>5</sub> Cl <sub>3</sub>
232.8	C <sub>14</sub> H <sub>29</sub> Cl	270.0	C <sub>10</sub> H <sub>4</sub> Cl <sub>4</sub>	388.9	C <sub>14</sub> H <sub>5</sub> Cl <sub>3</sub>
233.5	C <sub>7</sub> H <sub>11</sub> O <sub>2</sub> Cl <sub>3</sub>	274.9	C <sub>16</sub> H <sub>11</sub> OCl	403.8	C <sub>10</sub> Cl <sub>5</sub>
234.7	C <sub>11</sub> H <sub>9</sub> O <sub>2</sub> Cl	274.9	C <sub>17</sub> H <sub>25</sub> Cl	418.6	C <sub>4</sub> OCl <sub>10</sub>
235.0	C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	276.8	C <sub>4</sub> OCl <sub>5</sub>		
235.5	C <sub>8</sub> H <sub>5</sub> O <sub>2</sub> Cl <sub>3</sub>	276.9	C <sub>14</sub> H <sub>23</sub> OCl		
236.8	C <sub>2</sub> Cl <sub>4</sub>	278.4	C <sub>7</sub> HOCl <sub>5</sub>		
237.1	C <sub>13</sub> H <sub>10</sub> Cl <sub>2</sub>	278.8	C <sub>15</sub> H <sub>10</sub> Cl		
236.1	C <sub>10</sub> H <sub>15</sub> O <sub>2</sub> Cl <sub>2</sub>	280.8	C <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub>		
239.9	C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> Cl <sub>4</sub>	281.1	C <sub>14</sub> H <sub>10</sub> O <sub>2</sub> Cl <sub>3</sub>		
242.7	C <sub>14</sub> H <sub>7</sub> O <sub>2</sub> Cl	283.6	C <sub>11</sub> H <sub>7</sub> Cl <sub>2</sub>		
243.1	C <sub>8</sub> H <sub>15</sub> O <sub>4</sub> Cl <sub>2</sub>	284.8	C <sub>8</sub> Cl <sub>5</sub>		
243.9	C <sub>7</sub> H <sub>7</sub> OCl <sub>4</sub>	285.2	C <sub>3</sub> HCl <sub>7</sub>		



$C_4H_9Cl$ Contd.	1-Chloro-2,2-di- methylbutane..... 3:7590	$C_6H_{13}Cl$ Contd.	3-Chloro-2-methyl- pentane..... 3:7565
	4-Chloro-2,2-di- methylbutane..... 3:7555		4-Chloro-2-methyl- pentane..... 3:7495
$C_7H_{15}Cl$	1-Chloroheptane..... 3:8250		2-Chloro-3-methyl- pentane..... 3:9350
	1-Chloro-3-methyl- hexane..... 3:8155		3-Chloro-2,2-di- methylbutane..... 3:7475
	5-Chloro-2,3-di- methylpentane..... 3:8153	$C_7H_{15}Cl$	2-Chloroheptane..... 3:9432
$C_8H_{17}Cl$	1-Chlorooctane..... 3:8585		3-Chloroheptane..... 3:8080
	1-Chloro-2-ethyl- hexane..... 3:8370		4-Chloroheptane..... 3:8095
	1-Chloro-3-ethyl- hexane..... 3:8552		5-Chloro-2-methyl- hexane..... 3:7985
	1-Chloro-2-ethyl-3- methylpentane .... 3:9560		2-Chloro-3-methyl- hexane..... 3:9434
	1-Chloro-2,2,3,3-tetra- methylbutane..... 3:0945		4-Chloro-3-methyl- hexane..... 3:9436
$C_9H_{19}Cl$	1-Chlorononane..... 3:8719		2-Chloro-3-ethyl- pentane..... 3:9438
$C_{10}H_{21}Cl$	1-Chlorodecane..... 3:8785		4-Chloro-2,2-di- methylpentane..... 3:9440
	1-Chloro-3,7-di- methyloctane..... 3:9740	$C_8H_{17}Cl$	2-Chlorooctane..... 3:8378
$C_{11}H_{23}Cl$	1-Chloroundecane.... 3:8803		4-Chlorooctane..... 3:9538
$C_{12}H_{25}Cl$	1-Chlorododecane.... 3:8810		6-Chloro-2-methyl- heptane..... 3:9540
$C_{13}H_{27}Cl$	1-Chlorotridecane.... 3:9859		3-Chloro-4-methyl- heptane ..... 3:9548
$C_{14}H_{29}Cl$	1-Chlorotetradecane.. 3:9874		2-Chloro-3,4-di- methylhexane..... 3:9558
$C_{15}H_{31}Cl$	1-Chloropentadecane . 3:9890	$C_9H_{19}Cl$	2-Chlorononane..... 3:8635
$C_{16}H_{33}Cl$	1-Chlorohexadecane .. 3:0015		3-Chlorononane..... 3:9638
$C_{17}H_{35}Cl$	1-Chloroheptadecane . 3:0100		5-Chlorononane..... 3:9640
$C_{18}H_{37}Cl$	1-Chlorooctadecane.. 3:0095	3. With tertiary halogen	
2. With secondary halogen		$C_4H_9Cl$	<i>ter</i> -Butyl chloride..... 3:7045
$C_3H_7Cl$	2-Chloropropane..... 3:7025	$C_5H_{11}Cl$	<i>ter</i> -Amyl chloride..... 3:7220
$C_4H_9Cl$	2-Chlorobutane..... 3:7125	$C_6H_{13}Cl$	2-Chloro-2-methyl- pentane..... 3:7490
$C_5H_{11}Cl$	2-Chloropentane..... 3:7325		3-Chloro-3-methyl- pentane..... 3:7585
	3-Chloropentane..... 3:7330		2-Chloro-2,3-di- methylbutane..... 3:7600
	3-Chloro-2-methyl- butane..... 3:7275	$C_7H_{15}Cl$	2-Chloro-2-methyl- hexane..... 3:7945
$C_6H_{13}Cl$	2-Chlorohexane..... 3:7715		3-Chloro-3-methyl- hexane ..... 3:7950
	3-Chlorohexane..... 3:7670		

## B. DICHLORO DERIVATIVES.

1. *With both chlorine atoms primary.*
2.
  - a. Both chlorine atoms on same carbon.
  - b. Both chlorine atoms on different carbons.
3. *With both chlorine atoms tertiary.*
- 4.
- 5.
- 6.

## C. TRICHLORO DERIVATIVES.

- 1.
- 2.
- 3.
- 4.
- 5.
- 6.
- 7.

## D. TETRACHLORO DERIVATIVES.

1. *With all four chlorine atoms primary.*
- 2.
- 3.
- 4.
- 5.
6. *With two chlorine atoms primary, one secondary, and one tertiary.*

## E. PENTACHLORO DERIVATIVES.

1. *With all five chlorine atoms primary*
2. *With four chlorine atoms primary and one secondary*
3. *With three chlorine atoms primary and two secondary.*
4. *With two chlorine atoms primary and three secondary*
5. *With four chlorine atoms primary and one tertiary*

## F. HEXACHLORO DERIVATIVES

1. *With all six chlorine atoms primary*
2. *With five chlorine atoms primary and one secondary.*
3. *With four chlorine atoms primary and two secondary.*

## G. HEPTACHLORO DERIVATIVES.

## H. OCTACHLORO DERIVATIVES.

## UNIT 1. CHLORO SUBSTITUTION PRODUCTS OF SATURATED ACYCLIC HYDROCARBONS

A. Monochloro Derivatives		$C_6H_5Cl$	Isoamyl chloride.....	3:7365
1. <i>With primary halogen</i>		Contd	Neopentyl chloride...	3:7200
$CH_3Cl$	Methyl chloride.....			
$C_2H_5Cl$	Ethyl chloride.....	$C_6H_{13}Cl$	1-Chlorohexane.....	3:7955
$C_3H_7Cl$	n-Propyl chloride .		1-Chloro-2-methyl-	
			pentane . . . . .	3:7563
$C_4H_9Cl$	n-Butyl chloride. . .		5-Chloro-2-methyl-	
			pentane.....	3:7695
$C_4H_9Cl$	Isobutyl chloride .		1-Chloro-3-methyl-	
			pentane.....	3:0348
$C_5H_{11}Cl$	n-Amyl chloride		1-Chloro-2-ethyl-	
	sec.-Butylcarbinyl		butane .....	3:7720
	chloride . . . . .			
				3:7345

XII-630, XII<sub>1</sub>-(313)] via diazotization (9) (6) and reaction with alc. (9), or by reduction to 3,4,5-trichlorophenylhydrazine and reaction of this with Fehling soln. (poor yield (6)) (5), see indie. refs.; for prepn. of  $\bar{C}$  from 2,3-dichloroaniline [Beil. XII-621] (7) or from 2,6-dichloroaniline [Beil. XII-626] (7) (4) via diazotization and use of  $Cu_2Cl_2$  reaction see indie. refs.; for prepn. of  $\bar{C}$  from 4-chloro-3,5-diaminobenzenesulfonic acid-1 [Beil. XIV-718, XIV<sub>1</sub>-(727)] via conv. to 3,4,5-trichlorobenzenesulfonic acid-1 and subsequently hydrolyzing the sulfonic acid group see (1).]

[For formn. of  $\bar{C}$  (together with other prod.) from n mixt. of *o*- and *p*-dichlorobenzenes with  $Cl_2$  (10), or from *m*-dichlorobenzene +  $AlCl_3$  +  $Cl_2$  (11), or from  $\alpha$ -,  $\beta$ -, or  $\gamma$ -benzenehexachlorides with alc. KOH (5), or from  $\alpha$ -benzenehexachloride with pyridine or quinoline (5), see indie. refs.]

[ $\bar{C}$  with  $Cl_2$  in pres. of  $Al/Hg$  yields (9) exclusively 1,2,3,4-tetrachlorobenzene (3:0655), m.p. 44-45° (9);  $\bar{C}$  with liq.  $Cl_2$  in s.t. at room temp. for 7 days adds 6 atoms halogen yielding (12) 1,1',2,2',3,3',4,5,6-octachlorocyclohexane (1,2,3-trichlorobenzene hexachloride), pr. from MeOH, m.p. 80° (12).]

[ $\bar{C}$  on hydrolysis with steam at 550-800° over cat. yields (13) pyrogallol (1:1555); for behavior of  $\bar{C}$  with NaOMe in MeOH see (6) (14).]

$\bar{C}$  on mononitration, e.g., by soln. of  $\bar{C}$  (1 g.) in 5 ml. fuming  $HNO_3$  ( $D = 1.49$ ) (17), gives 100% yield (17) 1,2,3-trichloro-4-nitrobenzene [Beil. V-246], long colorless ndls. from alc., m.p. 56° (15) (7), 55-56° (17) (3) (note that the isomeric 1,2,3-trichloro-5-nitrobenzene [Beil. V-247, V<sub>1</sub>-(131)] has m.p. 72°).

$\bar{C}$  on dinitration, e.g.,  $\bar{C}$  (1 g.) refluxed 1 hr. with 5 ml. fuming  $HNO_3$  ( $D = 1.49$ ) + 5 ml. conc.  $H_2SO_4$ , then poured into aq. (17) (16), gives 100% yield 1,2,3-trichloro-4,6-dinitrobenzene, ndls. from hot alc., m.p. 92-93° (16) (17); this prod. (1 g.) htd. 1 hr. at 100° with 5 g. aniline as directed (17) yields 1,3-dianilino-2-chloro-4,6-dinitrobenzene, cryst. from  $C_6H_6$  or alc., m.p. 136-138° (17). [Note that an isomeric 1,2,3-trichloro-4,5-dinitrobenzene, cryst. from alc., m.p. 105-106° (16), has been obtd. by further nitration of 1,2,3-trichloro-5-nitrobenzene (mentioned in preceding paragraph).]

$\bar{C}$  with chlorosulfonic acid as directed (17) gives 1,2,3-trichlorobenzenesulfonyl chloride-4, m.p. 64-65° u.c. (17), 65-66° (2); this prod. with  $(NH_4)_2CO_3$  readily yields (17) 1,2,3-trichlorobenzenesulfonamide-4, m.p. 226-230° dec. u.c. (17).

3:0990 (1) I.G., Brit. 319,149, Oct. 10, 1929; French 661,490, July 25, 1929; *Cent.* 1930, I 740. (2) I.G., Brit. 287,178, May 9, 1928; *Cent.* 1929, II 352. (3) Beilstein, Kurbatow, *Ann.* 193, 234-235 (1878). (4) Dadieu, Pongratz, Kohlrausch, *Monatsh.* 61, 431-432 (1932). (5) van der Linden, *Ber.* 45, 231-247 (1912). (6) Holleman, *Rec. trav. chim.* 37, 196-201 (1918). (7) Körner, Contardi, *Atti accad. Lincei* (5) 18, I 100 (1904). (8) Zünderwerke E. Brünn, A. G., Ger. 570,460, Feb. 16, 1933; *Cent.* 1933, I 2770. (9) Cohen, Hartley, *J. Chem. Soc.* 87, 1365-1366 (1905). (10) Britton (to Dow Chem. Co.), U.S. 1,923,419, Aug. 22, 1933; *Cent.* 1933, II 3049; *C.A.* 27, 5086 (1933).

(12) van der Linden, *Rec. trav. chim.* March 15, 1932; *Cent.* 1932, I 2994; 779-780 (1931). (15) Holleman, (1921). (17) Hunt-

$C_7H_{15}Cl$ Contd.	3-Chloro-3-ethyl- pentane.....	3:8055
	2-Chloro-2,3-di- methylpentane .....	3:9442
	3-Chloro-2,3-di- methylpentane.....	3:7970
	2-Chloro-2,4-di- methylpentane.....	3:7750
	3-Chloro-2,2,3-tri- methylbutane ....	3:4020
$C_8H_{17}Cl$	2-Chloro-2-methyl- heptane.. . . .	3:8100
	3-Chloro-3-methyl- heptane.....	3:9544
	4-Chloro-4-methyl- heptane.....	3:9550
	3-Chloro-3-ethyl- hexane.....	3:8223
	3-Chloro-2,3-di- methylhexane.....	3:9554
	2-Chloro-2,5-di- methylhexane.....	3:9556
	3-Chloro-3-ethyl-2- methylpentane.....	3:8210
	4-Chloro-2,2,4-tri- methylpentane ...	3:8113
$C_9H_{19}Cl$	3-Chloro-3-methyl- octane.. . . .	3:9642
	4-Chloro-4-methyl- octane.....	3:9644
	3-Chloro-3-ethyl- heptane . . . . .	3:9646
	4-Chloro-4-ethyl- heptane... . . . .	3:9648
	3-Chloro-2,3-di- methylheptane . .	3:0650
	5-Chloro-2,5-di- methylheptane ..	3:9652
	3-Chloro-2,2,3-tri- methylhexane.....	3:9654
	3-Chloro-2,2-di- methyl-3-ethyl- pentane.....	3:9650
$C_{10}H_{21}Cl$	4-Chloro-4-methyl- nonane .. . . .	3:9730
	5-Chloro-5-methyl- nonane .....	3:9732
	3-Chloro-3-ethyl- octane.....	3:9734

$C_{10}H_{21}Cl$ Contd.	4-Chloro-4-ethyl- octane.....	3:9736
	3-Chloro-2,3-di- methyloctane.....	3:9738
	4-Chloro-4- <i>n</i> -propyl- heptane.....	3:9742
	4-Chloro-2,4,6-tri- methylheptane ....	3:9744

## B. Dichloro Derivatives

## 1. With both chlorine atoms primary

## a. Both chlorine atoms on same carbon

$CH_2Cl_2$	Methylene dichloride .	3:5020
$C_2H_4Cl_2$	1,1-Dichloroethane...	3:5035
$C_3H_6Cl_2$	1,1-Dichloropropane..	3:7230
$C_4H_8Cl_2$	1,1-Dichlorobutane ..	3:7550
	1,1-Dichloro-2-methyl- propane . . . . .	3:7425
$C_5H_{10}Cl_2$	1,1-Dichloropentane..	3:8015
	4,4-Dichloro-2-methyl- butane ....	3:7885
$C_7H_{14}Cl_2$	1,1-Dichloroheptane..	3:8650

## b. The two chlorine atoms on different carbons

$C_2H_4Cl_2$	1,2-Dichloroethane...	3:5130
$C_3H_6Cl_2$	1,3-Dichloropropane..	3:5450
$C_4H_8Cl_2$	1,4-Dichlorobutane	3:5835
	1,3-Dichloro-2-methyl- propane .. . . .	3:7960
$C_5H_{10}Cl_2$	1,5-Dichloropentane..	3:8575
	1,4-Dichloro-2-methyl- butane .....	3:8360
$C_6H_{12}Cl_2$	1,6-Dichlorohexane...	3:8720
$C_7H_{14}Cl_2$	1,7-Dichloroheptane..	3:9422
	1,5-Dichloro-3,3- dimethylpentane...	3:9430
$C_8H_{16}Cl_2$	1,8-Dichlorooctane...	3:8805
$C_9H_{18}Cl_2$	1,9-Dichlorononane...	3:8880
$C_{10}H_{20}Cl_2$	1,10-Dichlorodecane..	3:0720

## 2. With both chlorine atoms secondary

## a. Both chlorine atoms on same carbon

$C_3H_5Cl_2$  2,2-Dichloropropane... 3:7140

$C_4H_9Cl_2$  2,2-Dichlorobutane... 3:7415

$C_5H_{11}Cl_2$  2,2-Dichloropentane... 3:7755

3,3-Dichloropentane... 3:7895

3,3-Dichloro-2-methylbutane..... 3:9230

$C_6H_{13}Cl_2$  2,2-Dichlorohexane... 3:9342

3,3-Dichloro-2,2-dimethylbutane... 3:4325

4,4-Dichloro-2,2-dimethylbutane... 3:8132

$C_7H_{15}Cl_2$  2,2-Dichloroheptane... 3:9424

4,4-Dichloroheptane... 3:9426

3,3-Dichloro-2,4-dimethylpentane..... 3:7610

$C_8H_{17}Cl_2$  2,2-Dichlorooctane... 3:8670

3,3-Dichloro-2,2,4-trimethylpentane... 3:9530

## b. Both chlorine atoms on different carbons

$C_4H_9Cl_2$  *d,l*-2,3-Dichlorobutane... 3:7615

*meso*-2,3-Dichlorobutane... 3:7680

$C_5H_{11}Cl_2$  2,3-Dichloropentane... 3:8010

2,4-Dichloropentane... 3:8120

$C_6H_{13}Cl_2$  2,3-Dichlorohexane... 3:8300

2,5-Dichlorohexane... 3:8525

3,4-Dichlorohexane... 3:9344

## 3. With both chlorine atoms tertiary

$C_4H_9Cl_2$  2,3-Dichloro-2,3-dimethylbutane... 3:4520

$C_7H_{15}Cl_2$  2,4-Dichloro-2,4-dimethylpentane... 3:9128

$C_8H_{17}Cl_2$  2,5-Dichloro-2,5-dimethylhexane... 3:1550

3,4-Dichloro-3,4-dimethylhexane... 3:8315

$C_9H_{19}Cl_2$  2,6-Dichloro-2,6-dimethylheptane... 3:0455

$C_{10}H_{21}Cl_2$  2,7-Dichloro-2,7-dimethyloctane... 3:0840

3,4-Dichloro-3,4-dimethylhexane... 3:9724

## 4. With one chlorine primary and one secondary

$C_3H_7Cl_2$  1,2-Dichloropropane... 3:5200

$C_4H_9Cl_2$  1,2-Dichlorobutane... 3:7680

1,3-Dichlorobutane... 3:7925

$C_5H_{11}Cl_2$  1,2-Dichloropentane... 3:8140

1,3-Dichloropentane... 3:9220

1,4-Dichloropentane... 3:9224

1,3-Dichloro-2-methylbutane... 3:9228

3,4-Dichloro-2-methylbutane..... 3:8075

$C_6H_{13}Cl_2$  1,2-Dichlorohexane... 3:8380

1,5-Dichlorohexane... 3:9340

$C_7H_{15}Cl_2$  1,2-Dichloroheptane... 3:9420

1,2-Dichloro-4,4-dimethylpentane... 3:8516

$C_8H_{17}Cl_2$  1,6-Dichlorooctane... 3:9530

1,7-Dichlorooctane... 3:9532

4-Chloro-3-(chloromethyl)heptane... 3:9534

$C_9H_{19}Cl_2$  1,2-Dichlorononane... 3:9632

## 5. With one chlorine primary and one tertiary

$C_4H_9Cl_2$  1,2-Dichloro-2-methylpropane.... 3:7430

$C_5H_{11}Cl_2$  1,2-Dichloro-2-methylbutane..... 3:7920

2,4-Dichloro-2-methylbutane..... 3:8105

$C_6H_{13}Cl_2$  2,5-Dichloro-2-methylpentane..... 3:8540

## 6. With one chlorine secondary and one tertiary

$C_5H_{11}Cl_2$  2,3-Dichloro-2-methylbutane..... 3:7975

$C_6H_{13}Cl_2$  2,3-Dichloro-2-methylpentane..... 3:9346

## C. Trichloro Derivatives

## 1. With all three chlorine atoms primary

$CHCl_3$  Chloroform..... 3:5050

$C_2H_5Cl_3$  1,1,1-Trichloroethane.. 3:5085  
1,1,2-Trichloroethane. 3:5330

$C_3H_5Cl_3$  1,1,1-Trichloropropane 3:5270  
1,1,3-Trichloropropane 3:5660

$C_4H_9Cl_3$  4,4,4-Trichloro-2-methylbutane .... 3:9216

2. With two chlorine atoms primary and one secondary

$C_3H_5Cl_3$  1,1,2-Trichloropropane 3:5630  
1,2,3-Trichloropropane 3:5840

$C_4H_7Cl_3$  1,1,3-Trichlorobutane. 3:9086

$C_4H_9Cl_3$  1,3-Dichloro-2-(chloromethyl)butane .... 3:9218

3. With two chlorine atoms primary and one tertiary

$C_4H_7Cl_3$  1,1,2-Trichloro-2-methylpropane .... 3:5710  
1,2,3-Trichloro-2-methylpropane..... 3:5885

4. With one chlorine atom primary and two secondary

$C_3H_5Cl_3$  1,2,2-Trichloropropane 3:5475

$C_4H_7Cl_3$  1,2,3-Trichlorobutane 3:5935

5. With one chlorine each primary, secondary, and tertiary

$C_3H_5Cl_3$  1,2,3-Trichloro-2-methylbutane . . 3:6100

6. With all three chlorine atoms secondary

$C_4H_7Cl_3$  2,2,3-Trichlorobutane. 3:5680

7. With two chlorine atoms secondary and one tertiary

$C_4H_9Cl_3$  2,3,3-Trichloro-2-methylbutane . 3:4755

D. Tetrachloro Derivatives

1. With all four chlorine atoms primary

$CCl_4$  Carbon tetrachloride . 3:5100

$C_2H_2Cl_4$  1,1,1,2-Tetrachloroethane ... 3:5535

1,1,2,2-Tetrachloroethane... 3:5750

$C_3H_3Cl_4$  1,1,3-Trichloro-2-(chloromethyl)propane . .... 3:9084

$C_4H_5Cl_4$  1,3-Dichloro-2,2-bis-(chloromethyl)propane ..... 3:2657

2. With three chlorine atoms primary and one secondary

$C_2H_4Cl_4$  1,1,1,2-Tetrachloropropane. .... 3:5785

1,1,2,3-Tetrachloropropane ..... 3:6035

$C_4H_8Cl_4$  1,1,1,2-Tetrachlorobutane... 3:5622

3. With two chlorine atoms primary and two secondary

$C_3H_4Cl_4$  1,1,2,2-Tetrachloropropane ..... 3:5825

1,2,2,3-Tetrachloropropane .. ... 3:5895

$C_4H_8Cl_4$  1,2,3,4-Tetrachlorobutane (solid isomer) ..... 3:1760  
(liquid isomer)..... 3:9082

$C_6H_{10}Cl_4$  1,1,2,2-Tetrachlorohexane ..... 3:9332

4. With one chlorine atom primary and three secondary

$C_4H_8Cl_4$  1,2,2,3-Tetrachlorobutane . . . 3:0078

1,2,3,3-Tetrachlorobutane .. ... 3:9080

5. With three chlorine atoms primary and one tertiary

$C_4H_8Cl_4$  1,1,1,2-Tetrachloro-2-methylpropane 3:4725

1,1,2,3-Tetrachloro-2-methylpropane .. 3:6165

1,2,3-Trichloro-2-(chloromethyl)propane ... . 3:6335

6. With two chlorine atoms primary, one secondary, and one tertiary

$C_4H_8Cl_4$  1,2,3-Trichloro-2-(chloromethyl)butane . . . . 3:5230

E. Pentachloro Derivatives

1. With all five chlorine atoms primary

$C_2HCl_5$  Pentachloroethane.. 3:5880

2. With four chlorine atoms primary and one secondary

$C_4H_3Cl_5$  1,1,1,2,3-Pentachloropropane .. . 3:4740

1,1,2,3,3-Pentachloropropane... 3:6280

$C_6H_{11}Cl$	2-Chlorohexene-1 . . . .	3:7530
	3-Chlorohexene-3 . . . .	3:7535
	2-Chloro-3,3-dimethyl- butene-1 . . . . .	3:7340
$C_7H_{13}Cl$	2-Chloroheptene-1 . . . .	3:7938
	4-Chloroheptene-3 . . . .	3:8023
	3-Chloro-2,4-dimethyl- pentene-2 . . . . .	3:7605
$C_8H_{15}Cl$	2-Chlorooctene-1 . . . .	3:8346
	2-Chlorooctene-2 . . . .	3:8345
	4-Chlorooctene-4 . . . .	3:8230

2-Chloro-3-ethyl-3-  
methylpentene-1 . . . .

$C_{10}H_{19}Cl$	5-Chlorodecene-5 . . . .	3:9712
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$b_2$  DICHLORO

$C_3H_4Cl_2$	2,3-Dichloropropene-1	3:5190
$C_4H_6Cl_2$	2,3-Dichlorobutene-1 .	3:9074
	1,2-Dichlorobutene-2 (h-b) . . . . .	3:5615
	1,2-Dichlorobutene-2 (l-h) . . . . .	3:5360
	1,3-Dichlorobutene-2 .	3:5550

$C_5H_8Cl_2$	2,5-Dichloropentene-2	3:9202
	3,4-Dichloropentene-2	3:8045
	1,3-Dichloro-2-methyl- butene-2 . . . . .	3:8170

$b_2$  POLYCHLORO

$C_4H_6Cl_3$	1,2,4-Trichloro- butene-2 . . . . .	3:9062
	2,3,4-Trichloro- butene-2 . . . . .	3:9064
$C_4H_4Cl_4$	2,3,3,4-Tetrachloro- butene-1 . . . . .	3:9060

2. With two chlorine atoms on C attached  
to unsaturation

a. Both these chlorines are on same  
C atom

$C_2H_2Cl_2$	1,1-Dichloroethylene..	3:5005
$C_3H_4Cl_2$	1,1-Dichloropropene-1	3:5120
$C_4H_6Cl_2$	1,1-Dichloro-2-methyl- propene-1 . . . . .	3:5300
$C_2HCl_3$	1,1,2-Trichloro- ethylene . . . . .	3:5170

$C_3H_3Cl_3$	1,1,2-Trichloro- propene-1 . . . . .	3:5395
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$C_4H_5Cl_3$	1,1,3-Trichloro-2- methylpropene-1 . . . .	3:5025
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$C_6H_9Cl_3$	1,1,2-Trichloro- hexene-1 . . . . .	3:8326
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$C_2Cl_4$	Tetrachloroethylene . .	3:5460
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$C_5HCl_5$	1,1,2,3,3-Pentachloro- propene-1 . . . . .	3:6075
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$C_3Cl_6$	Hexachloropropene . . .	3:6370
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These two chlorines are on differ-  
ent carbons



$C_2H_2Cl_2$	<i>cis</i> -1,2-Dichloro- ethylene . . . . .	3:5042
	<i>trans</i> -1,2-Dichloro- ethylene . . . . .	3:5028

$C_3H_4Cl_2$	1,2-Dichloropro- pene-1 (h-b. isomer)	3:5150
	1,2-Dichloropropene-1 (l-b. isomer) . . . . .	3:5110

	<i>cis</i> -2,3-Dichloro- butene-2 . . . . .	3:5500
	<i>trans</i> -2,3-Dichloro- butene-2 . . . . .	3:7395

$C_6H_{10}Cl_2$	1,2-Dichlorohexene-1 .	3:9330
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$C_4HCl_3$	1,1,2-Trichloro- ethylene . . . . .	3:5170
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$C_3H_3Cl_3$	1,1,2-Trichloropro- pene-1 . . . . .	3:5395
	1,2,3-Trichloropro- pene-1 . . . . .	3:5050

$C_3H_2Cl_4$	1,2,3,3-Tetrachloro- propene-1 . . . . .	3:5920
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$C_4Cl_4$	Tetrachloroethylene . .	3:5460
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$C_6H_2Cl_4$	1,1,2,3,4,4-Hexa- chlorobutene-2 (liquid isomer) . . . . .	3:9046
	(solid isomer) . . . . .	3:1945

$C_6H_2Cl_6$	1,2,3,4,5,6-Hexa- chlorohexene-3 . . . . .	3:1220
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c. Polychloro			$C_6H_4Cl_2$	1-Chloro-2-(chloromethyl)-butadiene-1,3.....	3:9195
$C_4H_2Cl_3$	3,3,3-Trichloropropene-1.....	3:5345			
$C_4H_4Cl_2$	3,3,3-Trichloro-2-methylpropene-1...	3:5605	c. $C_8$ series		
$C_4H_5Cl_2$	1,1,1,4,4-Pentachlorobutene-2.....	3:9054	$C_8H_8Cl$	3-Chlorohexadiene-1,3	3:9312
$C_4H_7Cl_2$	Hexachlorobutene-X...	3:9048		1-Chloro-3-methylpentadiene-1,3....	3:9316
	Hexachlorobutene-Y...	3:9050		2-Chloro-3-methylpentadiene-1,3....	3:9318
B. Of Diolefins			$C_6H_8Cl_2$	1,3-Dichlorohexadiene-2,4.....	3:9310
1. With "cumulative" unsaturation			$C_6H_8Cl_4$	1,3,4,6-Tetrachlorohexadiene-2,4.....	3:9306
$C_4H_4Cl$	4-Chlorobutadiene-1,2	3:7225	"	d. $C_8$ series	
$C_4H_7Cl$	1-Chloro-3-methylbutadiene-1,2.....	3:7390	$C_8H_{12}Cl$	3-Chlorooctadiene-1,3	3:9506
$C_6H_8Cl$	1-Chloro-3-methylpentadiene-1,2....	3:9314	3. With "isolated" unsaturation		
$C_7H_{11}Cl$	1-Chloro-3-ethylpentadiene-1,2....	3:9406	$C_6H_7Cl_3$	3,3,6-Trichlorohexadiene-1,4 ...	3:9308
2. With "conjugated" unsaturation			$C_7H_{11}Cl$	4-Chloroheptadiene-1,6.....	3:9085
a. $C_4$ series			$C_8H_{10}Cl$	2-Chloro-6-methyl-5-methyleneheptene-2	3:9614
$C_4H_6Cl$	1-Chlorobutadiene-1,3	3:7219	C. Of Triolefins		
	2-Chlorobutadiene-1,3	3:7030	$C_6H_8Cl_2$	3,6-Dichlorohexatriene-1,3,4.....	3:9304
$C_4H_4Cl_2$	1,2-Dichlorobutadiene-1,3.....	3:9057	$C_6H_8Cl_3$	3,4,6-Trichlorohexatriene-1,2,4.....	3:9302
	2,3-Dichlorobutadiene-1,3....	3:5220	D. Of Tetraolefins		
$C_4H_5Cl_3$	1,2,3-Trichlorobutadiene-1,3.....	3:9052	$C_6H_6Cl$	3-Chlorohexatetraene-1,3,4,5....	3:7735
$C_4H_7Cl_4$	1,2,3,4-Tetrachlorobutadiene-1,3 (solid isomer).....	3:9870	$C_6H_4Cl_2$	3,4-Dichlorohexatetraene-1,2,4,5....	3:9300
	(liquid isomer).....	3:6160	E. Of Alkynes		
$C_4HCl_4$	1,1,2,3,4-Pentachlorobutadiene-1,3.....	3:9044	1. With chlorine attached to C also bearing triple bond		
$C_4Cl_6$	Hexachlorobutadiene-1,3.....	3:6425	a. Monochloro		
b. $C_5$ series			$C_5HCl$	Chloroacetylene.....	3:7000
$C_5H_7Cl$	3-Chloropentadiene-1,3.....	3:7360	$C_6H_5Cl$	1-Chlorohexyne-1....	3:9320
	1-Chloro-2-methylbutadiene-1,3.....	3:9200	$C_7H_9Cl$	1-Chloroheptyne-1....	3:8032
	3-Chloro-2-methylbutadiene-1,3....	3:7290		1-Chloro-3-ethylpentyne-1....	3:9410
	4-Chloro-2-methylbutadiene-1,3.....	3:7355	$C_8H_9Cl$	1-Chlorooctyne-1....	3:9510
			$C_9H_{11}Cl$	1-Chlorononyne-1....	3:9018

b. Dichloro  
 $C_2Cl_2$  Dichloroacetylene.... 3:5010

**2. With chlorine(s) attached to some C other than that bearing triple bond**

a. Monochloro

$B_1$  CHLORINE IS PRIMARY

$C_3H_3Cl$  3-Chloropropyne-1.... 3:7100

$C_4H_5Cl$  1-Chlorobutyne-2.... 3:7175

$C_8H_{13}Cl$  1-Chloro-octyne-2.... 3:9514

$B_2$  CHLORINE IS TERTIARY

$C_4H_7Cl$  3-Chloro-3-methylbutyne-1..... 3:7155

$C_5H_9Cl$  3-Chloro-3-methylpentyne-1.... 3:9322

4-Chloro-4-methylpentyne-2..... 3:9324

$C_8H_{15}Cl$  3-Chloro-3-methylheptyne-4..... 3:9516

$C_9H_{17}Cl$  2-Chloro-2-methyloctyne-3..... 3:9622

$C_{10}H_{19}Cl$  3-Chloro-3-methylnonyne-4. .... 3:9710

b. Dichloro

$C_8H_{13}Cl_2$  2,5-Dichloro-2,5-dimethylhexene-3.. 3:9504

F. Of Alkadi-yne

$C_4Cl_2$  1,4-Dichlorobutyne-1,3..... 3:9040

G. Of Alkenynes

$C_4H_5Cl$  1-Chlorobuten-3-yne-1 .. . . . . 3:7070

$C_7H_9Cl$  5-Chloro-5-methylhexen-1-yne-3 .. 3:9402

**UNIT 3. CHLORO SUBSTITUTION PRODUCTS OF HYDROCARBONS CONTAINING CYCLIC NUCLEI**

(Summary of Classification of Unit 3)

A. OF CYCLOALKANES.

B. OF MONONUCLEAR AROMATIC HYDROCARBONS.

1. With all chlorine in nucleus.
2. With all chlorine in side chain(s).
  - a. Saturated side chain(s).
  - b. Unsaturated side chain(s).
3. With chlorine both in ring and in side chain(s).

C. OF POLYNUCLEAR AROMATIC HYDROCARBONS.

1. With all chlorine in nucleus.
  - a. Systems with uncondensed rings.
  - b. Systems with condensed rings.
2. With all chlorine in side chain(s).
  - a. Systems with two uncondensed rings.
  - b. Systems with two condensed rings.
  - c. Systems with three uncondensed rings.
3. With chlorine both in nucleus and side chain.

**UNIT 3. CHLORO SUBSTITUTION PRODUCTS OF HYDROCARBONS CONTAINING CYCLIC NUCLEI**

A. Of Cycloalkanes

$C_5H_9Cl$  Chlorocyclopentane... 3:7545

$C_6H_{11}Cl$  Chlorocyclohexane.... 3:8040

$C_6H_9Cl_2$  *cis*-1,2,3,4,5,6-Hexachlorocyclohexane.. 3:4410

*trans*-1,2,3,4,5,6-Hexachlorocyclohexane.. 3:4990

B. Of Mononuclear Aromatic Hydrocarbons

1. With all chlorine in nucleus

$C_6H_5Cl$  Chlorobenzene..... 3:7903

$C_6H_4Cl_2$  *o*-Dichlorobenzene ... 3:6055

*m*-Dichlorobenzene ... 3:5960

*p*-Dichlorobenzene.... 3:0990

$C_6H_3Cl_3$	1,2,3-Trichlorobenzene	3:0990	$C_9H_{11}Cl$	2-Chloro-1,3,5-trimethylbenzene, . . .	3:8725
	1,2,4-Trichlorobenzene	3:6426	Contd.		
	1,3,5-Trichlorobenzene	3:1400	$C_{10}H_{13}Cl$	2-Chloro- <i>p</i> -cymene . .	3:8775
$C_6H_2Cl_4$	1,2,3,4-Tetrachlorobenzene . . . . .	3:0655		3-Chloro- <i>p</i> -cymene . .	3:8770
	1,2,3,5-Tetrachlorobenzene . . . . .	3:0915	<b>2. With all chlorine in side chain(s)</b>		
	1,2,4,5-Tetrachlorobenzene . . . . .	3:4115	<i>a. Saturated side chain(s)</i>		
$C_6HCl_5$	Pentachlorobenzene . .	3:2290	$C_7H_7Cl$	Benzyl chloride . . . . .	3:8535
$C_6Cl_6$	Hexachlorobenzene . .	3:4939	$C_7H_5Cl_2$	Benzal (di)chloride . .	3:6327
$C_7H_7Cl$	<i>o</i> -Chlorotoluene . . . . .	3:8245	$C_7H_3Cl_3$	Benzotrichloride . . . . .	3:6540
	<i>m</i> -Chlorotoluene . . . . .	3:8275	$C_8H_9Cl$	$\alpha$ -Chloroethylbenzene	3:8667
	<i>p</i> -Chlorotoluene . . . . .	3:8287		$\beta$ -Chloroethylbenzene .	3:8712
$C_7H_5Cl_2$	2,3-Dichlorotoluene . .	3:6345	$C_8H_3Cl_3$	$\alpha, \beta$ -Dichloroethylbenzene . . . . .	3:6685
	2,4-Dichlorotoluene . .	3:6290	$C_8H_9Cl$	<i>o</i> -Xylyl chloride . . . . .	3:8710
	2,5-Dichlorotoluene . .	3:6245		<i>m</i> -Xylyl chloride . . . . .	3:8700
	2,6-Dichlorotoluene . .	3:6270		<i>p</i> -Xylyl chloride . . . . .	3:8660
	3,4-Dichlorotoluene . .	3:6355	$C_8H_4Cl_2$	<i>o</i> -Xylylene (di)chloride . . . . .	3:1040
	3,5-Dichlorotoluene . .	3:6310		<i>m</i> -Xylylene (di)chloride . . . . .	3:0310
$C_7H_3Cl_3$	2,3,4-Trichlorotoluene	3:0425		<i>p</i> -Xylylene (di)chloride . . . . .	3:2825
	2,3,5-Trichlorotoluene	3:0610	$C_9H_{11}Cl$	$\gamma$ -Chloro- <i>n</i> -propylbenzene . . . . .	3:8777
	2,3,6-Trichlorotoluene	3:0625		$\alpha$ -Chloroisopropylbenzene . . . . .	3:9610
	2,4,5-Trichlorotoluene	3:2100	$C_{10}H_{13}Cl$	2,3,6-Trimethylbenzyl chloride . . . . .	3:9701
	2,4,6-Trichlorotoluene	3:0380		2,4,5-Trimethylbenzyl chloride . . . . .	3:9702
	3,4,5-Trichlorotoluene	3:0580		2,4,6-Trimethylbenzyl chloride . . . . .	3:0372
$C_7H_4Cl_4$	2,3,4,5-Tetrachlorotoluene . . . . .	3:2710		4-Isopropylbenzyl chloride . . . . .	3:8795
	2,3,4,6-Tetrachlorotoluene . . . . .	3:2480		$\beta$ -Chloro- <i>ter</i> -butylbenzene . . . . .	3:8780
	2,3,5,6-Tetrachlorotoluene . . . . .	3:2575	<i>b. Unsaturated side chain(s)</i>		
$C_7H_2Cl_5$	2,3,4,5,6-Pentachlorotoluene . . . . .	3:4937	$C_9H_5Cl$	$\omega$ -Chlorophenylacetylene . . . . .	3:9494
$C_8H_9Cl$	<i>o</i> -Chloro-ethylbenzene	3:8550		<i>o</i> -Chlorophenylacetylene . . . . .	3:0497
	<i>p</i> -Chloro-ethylbenzene	3:8570		<i>m</i> -Chlorophenylacetylene . . . . .	3:9500
	3-Chloro-1,2-dimethylbenzene . . . . .	3:8645		<i>p</i> -Chlorophenylacetylene . . . . .	3:0590
	4-Chloro-1,2-dimethylbenzene . . . . .	3:8675	$C_9H_7Cl$	$\alpha$ -Chlorovinylbenzene	3:8715
	2-Chloro-1,3-dimethylbenzene . . . . .	3:8590		$\beta$ -Chlorovinylbenzene .	3:8717
	4-Chloro-1,3-dimethylbenzene . . . . .	3:8665			
	5-Chloro-1,3-dimethylbenzene . . . . .	3:8640			
	2-Chloro-1,4-dimethylbenzene . . . . .	3:8600			
$C_9H_{11}Cl$	4-Chloro-isopropylbenzene . . . . .	3:8705			

$C_3H_5Cl$	1-Chloro-1-phenylpro- pene-1. ....	3:960f
	2-Chloro-1-phenylpro- pene-1. ....	3:960f
	3-Chloro-1-phenylpro- pene-1. ....	3:0010
	1-Chloro-2-phenylpro- pene-1. ....	3:8742
	1-Chloro-3-phenylpro- pene-1. ....	3:8737
	2-Chloro-3-phenylpro- pene-1. ....	3:9609

3. With chlorine both in ring and in side chain(s)

$C_7H_4Cl_4$	<i>o</i> -Chlorobenzyl chloride .....	3:6400
	<i>m</i> -Chlorobenzyl chloride .....	3:6445
	<i>p</i> -Chlorobenzyl chloride .....	3:0220

$C_7H_3Cl_5$	2,6-Dichlorobenzyl chloride ..	3:0410
	3,4-Dichlorobenzyl chloride .....	3:6795
	3,5-Dichlorobenzyl chloride .....	3:0350
	<i>o</i> -Chlorobenzal (di)chloride .....	3:6625
	<i>m</i> -Chlorobenzal (di)chloride .....	3:6710
	<i>p</i> -Chlorobenzal (di)chloride .....	3:0700

$C_7H_2Cl_6$	2,4-Dichlorobenzal (di)chloride .....	3:9399
	2,5-Dichlorobenzal (di)chloride ..	3:0490
	2,6-Dichlorobenzal (di)chloride .....	3:9399
	3,4-Dichlorobenzal (di)chloride .....	3:6867
	3,5-Dichlorobenzal (di)chloride .....	3:0370
	<i>o</i> -Chlorobenzotri- chloride .....	3:6880
	<i>m</i> -Chlorobenzotri- chloride .....	3:6845
	<i>p</i> -Chlorobenzotri- chloride .....	3:6825

$C_7H_3Cl_5$	2,3,4-Trichlorobenzal (di)chloride .....	3:2212
	2,3,6-Trichlorobenzal (di)chloride ..	3:2178

$C_7H_3Cl_5$ Contd.	2,4,5-Trichlorobenzal (di)chloride .....	3:6910
	2,4,6-Trichlorobenzal (di)chloride .....	3:0142

$C_7H_2Cl_6$	2,3,4,5-Tetrachloro- benzal (di)chloride .	3:9397
	2,3,4,6-Tetrachloro- benzal (di)chloride .	3:6980
	2,3,5,6-Tetrachloro- benzal (di)chloride .	3:6980

$C_7HCl_6$	Pentachlorobenzal (di)chloride .....	3:3590
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C. Of Polynuclear Aromatic Hydrocarbons

1. With all chlorine in nucleus

a. Systems with uncondensed rings

$C_{12}H_8Cl_2$	2-Chlorobiphenyl ..	3:0300
	3-Chlorobiphenyl ..	3:8910
	4-Chlorobiphenyl ....	3:1912

$C_{12}H_6Cl_4$	2,2'-Dichlorobiphenyl.	3:1325
	2,3-Dichlorobiphenyl	3:9850
	2,4'-Dichlorobiphenyl	3:0670
	2,5-Dichlorobiphenyl .	3:9854
	3,3'-Dichlorobiphenyl	3:0180
	3,4-Dichlorobiphenyl .	3:0685
	3,5-Dichlorobiphenyl .	3:0360
	4,4'-Dichlorobiphenyl.	3:4300

$C_{12}H_{10}Cl_2$	4,4'-Dichlorodiphenyl- methane....	3:1057
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$C_{14}H_{10}Cl_2$	1,1-Di-( <i>p</i> -chloro- phenyl)ethylene ...	3:2475
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$C_{14}H_{12}Cl_2$	1,1-Di-( <i>p</i> -chloro- phenyl)ethane....	3:0995
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b. Systems with condensed rings

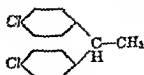
$C_{10}H_7Cl$	1-Chloronaphthalene .	3:6878
	2-Chloronaphthalene .	3:1285

$C_{10}H_5Cl_5$	1,2-Dichloronaphtha- lene. ....	3:0320
	1,3-Dichloronaphtha- lene....	3:1310
	1,4-Dichloronaphtha- lene ..	3:1655
	1,5-Dichloronaphtha- lene.....	3:3200
	1,6-Dichloronaphtha- lene.....	3:0810
	1,7-Dichloronaphtha- lene.....	3:1385
	1,8-Dichloronaphtha- lene .....	3:2435
	2,3-Dichloronaphtha- lene ..	3:3665
	2,6-Dichloronaphtha- lene....	3:4040
	2,7-Dichloronaphtha- lene.....	3:3445

$C_{10}H_5Cl_3$	1,2,3-Trichloro-naphthalene.....	3:2125	$C_{24}H_{12}Cl_3$	1,1,1-Trichloro-2,2-diphenylethane....	3:1420
	1,2,4-Trichloro-naphthalene.....	3:2490	$C_{14}H_{10}Cl_4$	1,1,2,2-Tetrachloro-1,2-diphenylethane...	3:4496
	1,2,5-Trichloro-naphthalene.....	3:1930 <sup>1</sup>	$C_{24}H_{10}Cl_2$	<i>cis</i> -1,2-Dichloro-1,2-diphenylethylene ..	3:1350
	1,2,6-Trichloro-naphthalene.....	3:2515		<i>trans</i> -1,2-Dichloro-1,2-diphenylethylene.....	3:4210
	1,2,7-Trichloro-naphthalene.....	3:2325		1,1-Dichloro-2,2-diphenylethylene.....	3:1938
	1,2,8-Trichloro-naphthalene.....	3:2220	b. Systems with two condensed rings		
	1,3,5-Trichloro-naphthalene.....	3:3015	$C_{24}H_9Cl$	1-(Chloromethyl)-naphthalene.....	3:0250
	1,3,6-Trichloro-naphthalene.....	3:1975		2-(Chloromethyl)-naphthalene.....	3:0747
	1,3,7-Trichloro-naphthalene.....	3:3400	c. Systems with three uncondensed rings		
	1,3,8-Trichloro-naphthalene.....	3:2420	$C_{19}H_{11}Cl$	$\alpha$ -Chlorotriphenylmethane.....	3:3410
	1,4,5-Trichloro-naphthalene.....	3:4005	$C_{20}H_{11}Cl$	1-Chloro-1,2,2-triphenylethylene ..	3:3560
	1,4,6-Trichloro-naphthalene .....	3:1625	3. With chlorine both in nucleus and in side chain		
	2,3,5-Trichloro-naphthalene.....	3:3300	$C_{14}H_{10}Cl_4$	1,1-Dichloro-2,2-bis-( <i>p</i> -chlorophenyl)ethane.....	3:3320
	2,3,6-Trichloro-naphthalene.....	3:2455		1,1-Dichloro-2-( <i>o</i> -chlorophenyl)-2-( <i>p</i> -chlorophenyl)ethane.....	3:1890
$C_{18}Cl_8$	Octachloronaphthalene.....	3:4893	$C_{14}H_9Cl_5$	1,1,1-Trichloro-2,2-bis-( <i>o</i> -chlorophenyl)ethane.....	3:9865
$C_{10}H_5Cl_4$	1,2,3,4-Tetrachloro-1,2,3,4-tetrahydronaphthalene.....	3:4750		1,1,1-Trichloro-2,2-bis-( <i>p</i> -chlorophenyl)ethane.....	3:3298
	5,6,7,8-Tetrachloro-1,2,3,4-tetrahydronaphthalene.....	3:4703		1,1,1-Trichloro-2-( <i>o</i> -chlorophenyl)-2-( <i>p</i> -chlorophenyl)ethane.....	3:1820
$C_{14}H_5Cl_2$	9,10-Dichloroanthracene.....	3:4916		1,1,1-Trichloro-2-( <i>m</i> -chlorophenyl)-2-( <i>p</i> -chlorophenyl)ethane.....	3:9867
2. With all chlorine in side chain(s)					
a. Systems with two uncondensed rings					
$C_{13}H_{11}Cl$	$\alpha$ -Chlorodiphenylmethane...	3:0060	$C_{14}H_9Cl_5$	1,1,1-Trichloro-2,2-bis-( <i>o</i> -chlorophenyl)ethane.....	3:9865
$C_{13}H_{10}Cl_2$	$\alpha,\alpha$ -Dichlorodiphenylmethane...	3:6960		1,1,1-Trichloro-2-( <i>o</i> -chlorophenyl)-2-( <i>p</i> -chlorophenyl)ethane.....	3:1820
$C_{14}H_{13}Cl$	1,1-Diphenylethyl chloride.....	3:9870		1,1,1-Trichloro-2-( <i>m</i> -chlorophenyl)-2-( <i>p</i> -chlorophenyl)ethane.....	3:9867
	2,2-Diphenylethyl chloride.....	3:9871	$C_{14}H_9Cl_5$	1,1,1,2-Tetrachloro-2-bis-( <i>p</i> -chlorophenyl)ethane.....	3:2477
$C_{14}H_{13}Cl_2$	<i>di</i> -1,2-Dichloro-1,2-diphenylethane.....	3:2570			
	<i>meso</i> -1,2-Dichloro-1,2-diphenylethane.....	3:4854			
	1,1-Dichloro-2,2-diphenylethane.....	3:1940			

3:0993 1,1-Di-(*p*-CHLOROPHENYL)ETHANE $C_{14}H_{12}Cl_2$ 

Beil. S.N. 470



M.P. 51-55° (1)      B.P. 143-145° at 2 mm. (1)

Colorless cryst. from 90% AcOH. — Note that, when pure, neither solid  $\bar{C}$  nor its solns. show any fluorescence either in visible or ultraviolet light. (1). — Note also that, although m.p. of  $\bar{C}$  is identical with that of its next lower homolog, viz., di-(*p*-chlorophenyl)methane (4,4'-dichlorodiphenylmethane) (3:1057), nevertheless the m.p. of their mixture is depressed to 40-50° (1).

[For prepn. of  $\bar{C}$  from 1,1-di-(*p*-chlorophenyl)ethylene (3:2475) by cat. hydrogenation (62% yield) see (1); for formn. of  $\bar{C}$  from chlorobenzene (3:7903) with acetylene in presence of  $AlCl_3$  see (2), but note that by this method various undetermined impurities which show blue fluorescence are also formed (1).]

$\bar{C}$  on oxidn. with  $CrO_2/AcOH$  + trace of  $H_2SO_4$  gives (1) 4,4'-dichlorobenzophenone (3:4270), m.p. 112-113°.

$\bar{C}$  does not (1) yield an addn. prod. with  $PhOH$ .

3:0995 (1) Grummitt, Buck, Becker, *J. Am. Chem. Soc.* 67, 2265-2266 (1945). (2) Cook, Chambers, *J. Am. Chem. Soc.* 43, 335 (1921).

## UNIT 4. CHLORO SUBSTITUTION PRODUCTS OF HYDROXY COMPOUNDS

## A. Of Alcohols

## 1. Of acyclic alcohols

## a. Saturated monohydric

 $s_1$  PRIMARY $C_2H_5OCl$  2-Chloroethanol-1.... 3:5552 $C_2H_4OCl_2$  2,2-Dichloroethanol-1, 3:5745 $C_2H_5OCl_2$  2,2,2-Trichloroethanol-1 ..... 3:5775 $C_3H_7OCl$  2-Chloropropanol-1... 3:7917  
3-Chloropropanol-1... 3:8285 $C_3H_5OCl_2$  2,3-Dichloropropanol-1.. ..... 3:6060 $C_4H_9OCl$  2-Chlorobutanol-1... 3:9160  
3-Chlorobutanol-1... 3:9165  
4-Chlorobutanol-1... 3:9170 $C_4H_7OCl_3$  2,2,3-Trichlorobutanol-1..... 3:1330 $C_4H_9OCl$  2-Chloro-2-methylpropanol-1... ..... 3:7905  
3-Chloro-2-methylpropanol-1 ..... 3:9180 $C_5H_{11}OCl$  5-Chloropentanol-1... 3:9295 $C_6H_{13}OCl$  6-Chlorohexanol-1... 3:9395 $C_7H_{15}OCl$  7-Chloroheptanol-1... 3:0013 $C_8H_{17}OCl$  8-Chlorooctanol-1... 3:9590 $C_9H_{19}OCl$  9-Chlorononanol-1... 3:0170 $C_{10}H_{21}OCl$  10-Chlorodecanol-1... 3:0014 $C_{12}H_{25}OCl$  12-Chlorododecanol-1 ..... 3:0172 $C_{14}H_{29}OCl$  14-Chlorotetradecanol-1..... 3:0375 $C_{16}H_{33}OCl$  16-Chlorohexadecanol-1..... 3:0525 $C_{18}H_{37}OCl$  18-Chlorooctadecanol-1..... 3:0985 $s_2$  SECONDARY $C_3H_7OCl$  1-Chloropropanol-2... 3:7747 $C_3H_5OCl_2$  1,1-Dichloropropanol-2..... 3:5755  
1,3-Dichloropropanol-2..... 3:5985 $C_3H_5OCl_2$  1,1,1-Trichloropropanol-2..... 3:0846 $C_3H_4OCl_4$  1,1,1,3-Tetrachloropropanol-2..... 3:9036

1,1,3,3-Tetrachloropropanol-2..... 3:9037

 $C_4H_9OCl$  1-Chlorobutanol-2.... 3:8025  
3-Chlorobutanol-2.... 3:8000*erythro*-3-Chlorobutanol-2..... 3:8004  
*threo*-3-Chlorobutanol-2..... 3:8002

4-Chlorobutanol-2.... 3:9175

 $C_4H_9OCl_2$  1,3-Dichlorobutanol-2 3:9145

1,1-Dichloro-2-methylpropanol-2..... 3:5772

 $C_4H_7OCl_3$  1,1,1-Trichlorobutanol-2 ..... 3:5955 $C_5H_{11}OCl$  1-Chloropentanol-2... 3:8225  
1-Chloropentanol-3... 3:8500

2-Chloro-2-methylbutanol-3..... 3:9290

 $s_3$  TERTIARY $C_4H_9OCl$  1-Chloro-2-methylpropanol-2..... 3:7752 $C_4H_8OCl_2$  1,3-Dichloro-2-methylpropanol-2..... 3:5977 $C_4H_7OCl_3$  1,1,1-Trichloro-2-methylpropanol-2 . 3:2662 $C_5H_{11}OCl$  1-Chloro-2-methylbutanol-2..... 3:8175

3-Chloro-2-methylbutanol-2..... 3:8030

4-Chloro-2-methylbutanol-2..... 3:8335

## b. Saturated dihydric

 $C_3H_7O_2Cl$  3-Chloropropanediol-1,2... ..... 3:9038

2-Chloropropanediol-1,3 ..... 3:9039

 $C_4H_9O_2Cl$  3-Chloro-2-methylpropanediol-1,2.... 3:0190

## c. Unsaturated (olefinic) monohydric

 $s_1$  PRIMARY $C_3H_5OCl$  2-Chloropropen-2-ol-1. 3:5635

3-Chloropropen-2-ol-1. 3:5620

$C_{14}H_9Cl_3$	1-Chloro-2,2-bis-(p-chlorophenyl)-ethylene. . . . .	3:1430	$C_{14}H_9Cl_4$ Contd.	1,1-Dichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)-ethylene . . . . .	3:1925
$C_{14}H_9Cl_4$	1,1-Dichloro-2,2-bis-(p-chlorophenyl)-ethylene . . . . .	3:2438		1,1-Dichloro-2-(m-chlorophenyl)-2-(p-chlorophenyl)-ethylene . . . . .	3:9863

## UNIT 4. CHLORO SUBSTITUTION PRODUCTS OF HYDROXY COMPOUNDS

(Summary of Classification of Unit 4)

## A. OF ALCOHOLS

## 1. Of acyclic alcohols.

## a. Saturated monohydric.

a<sub>1</sub> Primary.a<sub>2</sub> Secondary.a<sub>3</sub> Tertiary.

## b. Saturated dihydric.

## c. Unsaturated (olefinic) monohydric.

c<sub>1</sub> Primary.c<sub>2</sub> Secondary.

## 2. Of cyclanols (alicyclic alcohols).

## 3. Of aromatic alcohols.

## 4. Of alcohols containing also other functional groups.

a. Ether/alcohols.

b. Ester/alcohols.

c. Ether/ester/alcohols.

d. Acid/alcohols (hydroxy acids).

## B. OF PHENOLS.

## 1. Of mononuclear phenols.

## a. Monohydric.

a<sub>1</sub> Derivatives of phenol.a<sub>2</sub> Derivatives of methylphenols.a<sub>3</sub> Derivatives of xylenols.a<sub>4</sub> Derivatives of miscellaneous alkylphenols.a<sub>5</sub> Derivatives of phenolic aldehydes.a<sub>6</sub> Derivatives of phenolic acids.a<sub>7</sub> Derivatives of phenolic acid chlorides.

## b. Dihydric.

b<sub>1</sub> Derivatives of pyrocatechol.b<sub>2</sub> Derivatives of resorcinol.b<sub>3</sub> Derivatives of hydroquinone.

## c. Trihydric.

## 2. Of binuclear phenols.

## a. Monohydric.

a<sub>1</sub> With uncondensed rings.a<sub>2</sub> With condensed rings.



$C_7H_5OCl_3$  2,4,6-Trichloro-3-methylphenol..... 3:0618

$C_7H_7OCl$  2-Chloro-4-methylphenol..... 3:6215  
3-Chloro-4-methylphenol..... 3:1025

$C_7H_5OCl_2$  2,6-Dichloro-4-methylphenol..... 3:0400

#### $a_3$ DERIVATIVES OF THE XYLENOLS

$C_8H_9OCl$  5-Chloro-*o*-3-xlenol.. 3:2115  
6-Chloro-*o*-3-xlenol.. 3:2218  
3-Chloro-*o*-4-xlenol.. 3:0158  
5-Chloro-*o*-4-xlenol.. 3:1754  
6-Chloro-*o*-4-xlenol.. 3:2705

5-Chloro-*m*-4-xlenol . 3:8784  
6-Chloro-*m*-4-xlenol . 3:2460

2-Chloro-*m*-5-xlenol . 3:3505  
5-Chloro-*m*-5-xlenol . 3:2180  
6-Chloro-*m*-5-xlenol . 3:0844  
5-Chloro-*p*-2-xlenol.. 3:1822

$C_8H_9OCl_2$  4,5-Dichloro-*o*-3-xlenol..... 3:2442

3,5-Dichloro-*o*-4-xlenol..... 3:0935

3,6-Dichloro-*o*-4-xlenol..... 3:2216

5,6-Dichloro-*o*-4-xlenol..... 3:3005

2,4-Dichloro-*m*-5-xlenol..... 3:2182

2,6-Dichloro-*m*-5-xlenol..... 3:2638

$C_8H_7OCl_3$  Trichloro-*o*-3-xlenol . 3:4742

Trichloro-*o*-4-xlenol . 3:4747

Trichloro-*m*-4-xlenol . 3:4707

Trichloro-*m*-5-xlenol . 3:4713

Trichloro-*p*-xlenol... 3:4709

#### DERIVATIVES OF MISCELLANEOUS ALKYLPHENOLS

$C_{10}H_{13}OCl$  2-Chloro-4-*n*-butylphenol..... 3:8830

2-Chloro-4-*ter*-butylphenol..... 3:9760

*p*-Chlorocaryacrol.... 3:0480

*p*-Chlorothymol..... 3:1293

#### $a_3$ DERIVATIVES OF PHENOLIC ALDEHYDES

$C_7H_5O_2Cl$  3-Chloro-2-hydroxybenzaldehyde..... 3:1010

4-Chloro-2-hydroxybenzaldehyde..... 3:0960

5-Chloro-2-hydroxybenzaldehyde..... 3:2800

$C_7H_5O_2Cl_2$  3,5-Dichloro-2-hydroxybenzaldehyde. 3:2637

$C_7H_5O_2Cl$  2-Chloro-3-hydroxybenzaldehyde..... 3:4085

4-Chloro-3-hydroxybenzaldehyde..... 3:3780

6-Chloro-3-hydroxybenzaldehyde..... 3:3350

$C_7H_5O_2Cl_2$  2,4-Dichloro-3-hydroxybenzaldehyde. 3:4140

2,6-Dichloro-3-hydroxybenzaldehyde. 3:4160

4,6-Dichloro-3-hydroxybenzaldehyde. 3:3952

$C_7H_5O_2Cl_3$  2,4,6-Trichloro-3-hydroxybenzaldehyde. 3:3520

$C_7H_5O_2Cl$  2-Chloro-4-hydroxybenzaldehyde..... 3:4280

3-Chloro-4-hydroxybenzaldehyde..... 3:4065

3,5-Dichloro-4-hydroxybenzaldehyde 3:4400

#### $a_3$ DERIVATIVES OF PHENOLIC ACIDS

$C_7H_5O_3Cl$  3-Chloro-2-hydroxybenzoic acid..... 3:4745

4-Chloro-2-hydroxybenzoic acid..... 3:4908

5-Chloro-2-hydroxybenzoic acid..... 3:4705

6-Chloro-2-hydroxybenzoic acid..... 3:4610

$C_7H_5O_3Cl_2$  3,6-Dichloro-2-hydroxybenzoic acid.. 3:4935

$C_7H_5O_3Cl$  2-Chloro-3-hydroxybenzoic acid..... 3:4395

4-Chloro-3-hydroxybenzoic acid..... 3:4933

6-Chloro-3-hydroxybenzoic acid..... 3:4720

$C_7H_5O_3Cl$  2-Chloro-4-hydroxybenzoic acid..... 3:4430

3-Chloro-4-hydroxybenzoic acid..... 3:4675

3,5-Dichloro-4-hydroxybenzoic acid.. 3:4950

$C_4H_7OCl$	2-Chlorohuten-2-ol-1..	3:8240
	3-Chlorohuten-2-ol-1..	3:8270
	4-Chlorohuten-2-ol-1..	3:9114
	2-Chlorohuten-3-ol-1..	3:0113
	3-Chloro-2-methyl- propen-2-ol-1.....	3:8340

$C_2$  SECONDARY

$C_4H_7OCl$	1-Chlorohuten-3-ol-2..	3:8110
	3-Chlorohuten-3-ol-2..	3:9115

2. Of cyclanols (alicyclic alcohols)

$C_6H_{11}OCl$	cis-2-Chlorocyclo- hexanol-1.....	3:9374
	trans-2-Chlorocyclo- hexanol-1.....	3:0175
	4-Chlorocyclo- hexanol-1.....	3:9376

3. Of aromatic alcohols

$C_8H_9OCl$	Styrene chlorohydrin..	3:9570
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4. Of alcohols containing also other functional groups

a. Ether/alcohols

$C_4H_7O_2Cl$	2-( $\beta$ -Chloroethoxy)- ethanol-1.....	3:9185
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b. Ester/alcohols

$C_4H_7O_2Cl$	$\beta$ -Hydroxyethyl chloroacetate.....	3:6780
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$C_4H_7O_2Cl_2$	$\beta$ -Hydroxyethyl di- chloroacetate.....	3:0107
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$C_4H_7O_2Cl_3$	$\beta$ -Hydroxyethyl tri- chloroacetate.....	3:9099
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$C_4H_7O_2Cl$	$\beta$ -Chloro- $\gamma$ -hydroxy- n-propyl acetate..	3:6648
	$\gamma$ -Chloro- $\beta$ -hydroxy- n-propyl acetate....	3:6775
	$\beta$ -Chloro- $\beta'$ -hydroxy- isopropyl acetate..	3:6517

c. Ether/ester alcohols

$C_6H_{11}O_4Cl$	Diethylene glycol mono(chloroacetate)	3:9390
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$C_6H_{11}O_4Cl$	Triethylene glycol mono(chloroacetate)	3:9588
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d. Acid/alcohols

$C_4H_7O_2Cl_2$	$\beta\beta$ -Dichloro- $\alpha$ - hydroxyisobutyric acid.....	3:2145
	$\beta\beta'$ -Dichloro- $\alpha$ - hydroxyisobutyric acid.....	3:2565

B. Of Phenols

1. Mononuclear phenols

a. Monohydric

$A_1$  DERIVATIVES OF PHENOL

$C_6H_5OCl$	<i>o</i> -Chlorophenol.....	3:5980
	<i>m</i> -Chlorophenol.....	3:0255
	<i>p</i> -Chlorophenol.....	3:0475

$C_6H_4OCl_2$	2,3-Dichlorophenol..	3:1175
	2,4-Dichlorophenol..	3:0560
	2,5-Dichlorophenol..	3:1190
	2,6-Dichlorophenol..	3:1595
	3,4-Dichlorophenol..	3:1460
	3,5-Dichlorophenol..	3:1670

$C_6H_3OCl_3$	2,3,4-Trichlorophenol..	3:2185
	2,3,5-Trichlorophenol..	3:1340
	2,3,6-Trichlorophenol..	3:1160
	2,4,5-Trichlorophenol..	3:1620
	2,4,6-Trichlorophenol..	3:1673
	3,4,5-Trichlorophenol..	3:2885

$C_6H_2OCl_4$	2,3,4,5-Tetrachloro- phenol.....	3:3523
	2,3,4,6-Tetrachloro- phenol.....	3:1687
	2,3,5,6-Tetrachloro- phenol.....	3:3460

$C_6HOCl_5$	Pentachlorophenol....	3:4850
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$A_2$  DERIVATIVES OF THE METHYL-  
PHENOLS (CRESOLS)

$C_7H_7OCl$	3-Chloro-2-methyl- phenol.....	3:2280
	4-Chloro-2-methyl- phenol.....	3:0780
	5-Chloro-2-methyl- phenol.....	3:1815
	6-Chloro-2-methyl- phenol.....	3:8615

$C_7H_6OCl_2$	4,5-Dichloro-2- methylphenol.....	3:2910
	4,6-Dichloro-2- methylphenol.....	3:1020

$C_7H_7OCl$	2-Chloro-3-methyl- phenol.....	3:1055
	4-Chloro-3-methyl- phenol.....	3:1535
	6-Chloro-3-methyl- phenol.....	3:0700

$C_7H_6OCl_2$	2,4-Dichloro-3- methylphenol.....	3:1205
	2,6-Dichloro-3- methylphenol.....	3:0150
	4,6-Dichloro-3- methylphenol.....	3:1745

# UNIT 5. CHLORO SUBSTITUTION PRODUCTS OF CARBONYL COMPOUNDS (AND THEIR RELATIVES)

(Summary of Classification of Unit 5)

## A. OF ALDEHYDES.

1. *Acyclic aldehydes.*

a. Saturated.

b. Unsaturated.

c. Relatives of the above.

c<sub>1</sub> Hydrates.c<sub>2</sub> Hemiacetals.c<sub>3</sub> Diethylacetals.c<sub>4</sub> Acetals with chlorine only in alcohol radicals;c<sub>5</sub> Polymers.2. *Aromatic aldehydes.*

a. Simple aldehydes.

b. Phenolic aldehydes.

## B. OF KETONES.

1. *Dialkyl ketones.*2. *Alcyclic ketones.*3. *Alkyl aryl ketones.*

a. With chlorine only in alkyl.

b. With chlorine both in alkyl and aryl.

c. With chlorine only in aryl.

4. *Diaryl ketones.*5. *Ketones containing also other functional groups.*

a. Keto-acid chlorides.

b. Keto-acid esters.

## C. OF QUINONES.

1. *Mononuclear quinones.*2. *Dinuclear quinones.*3. *Trinuclear quinones.*

# UNIT 5. CHLORO SUBSTITUTION PRODUCTS OF CARBONYL COMPOUNDS (AND THEIR RELATIVES)

## A. Of Aldehydes

1. *Acyclic Aldehydes*

a. Saturated

C<sub>2</sub>H<sub>3</sub>OCl Chloroacetaldehyde... 3:7212C<sub>2</sub>H<sub>2</sub>OCl<sub>2</sub> Dichloroacetaldehyde. 3:5180C<sub>3</sub>HOCl<sub>3</sub> Trichloroacetaldehyde 3:5210C<sub>3</sub>H<sub>4</sub>OCl α-Chloropropionalde-

hyde..... 3:5160

β-Chloropropionalde-

hyde..... 3:5576

C<sub>3</sub>H<sub>4</sub>OCl<sub>2</sub> α,α-Dichloropropion-

aldehyde..... 3:9033-A

α,β-Dichloropropion-

aldehyde..... 3:9034

C<sub>3</sub>H<sub>3</sub>OCl<sub>3</sub> α,α,β-Trichloropro-

pionaldehyde..... 3:9033

C<sub>4</sub>H<sub>7</sub>OCl

α-Chloro-n-

butyraldehyde..... 3:9109

β-Chloro-n-

butyraldehyde..... 3:9110

γ-Chloro-n-

butyraldehyde..... 3:9111

C<sub>4</sub>H<sub>5</sub>OCl<sub>2</sub>

α,β-Dichloro-n-

butyraldehyde..... 3:9102

C<sub>4</sub>H<sub>3</sub>OCl<sub>3</sub>

α,α,β-Trichloro-n-

butyraldehyde..... 3:5910

α,α,γ-Trichloro-n-

butyraldehyde..... 3:9094

C<sub>4</sub>H<sub>7</sub>OCl

α-Chloro-iso-

butyraldehyde..... 3:7235

β-Chloro-iso-

butyraldehyde..... 3:9112

a<sub>7</sub> PHENOLIC ACID CHLORIDES

$C_7H_5O_2Cl$	2-Hydroxybenzoyl chloride . . . . .	3:0085
	3-Hydroxybenzoyl chloride . . . . .	3:9446
	4-Hydroxybenzoyl chloride . . . . .	3:9447

## b. Dihydric

b<sub>1</sub> DERIVATIVES OF PYROCATECHOL

$C_6H_4O_2Cl$	3-Chlorocatechol . . . . .	3:0745
	4-Chlorocatechol . . . . .	3:2470
$C_6H_4O_2Cl_2$	3,5-Dichlorocatechol . . . . .	3:2192
	4,5-Dichlorocatechol . . . . .	3:3525
$C_6H_3O_2Cl_3$	3,4,5-Trichlorocatechol . . . . .	3:3448
$C_6H_2O_2Cl_4$	Tetrachlorocatechol . . . . .	3:4875

b<sub>2</sub> DERIVATIVES OF RESORCINOL

$C_6H_4O_2Cl$	2-Chlororesorcinol . . . . .	3:2690
	4-Chlororesorcinol . . . . .	3:3100
	5-Chlororesorcinol . . . . .	3:3530
$C_6H_4O_2Cl_2$	4,6-Dichlororesorcinol . . . . .	3:3390
$C_6H_3O_2Cl_3$	2,4,6-Trichlororesorcinol . . . . .	3:2174
$C_6H_2O_2Cl_4$	Tetrachlororesorcinol . . . . .	3:4135

b<sub>3</sub> DERIVATIVES OF HYDROQUINONE

$C_6H_4O_2Cl$	2-Chlorohydroquinone . . . . .	3:3130
$C_6H_4O_2Cl_2$	2,3-Dichlorohydroquinone . . . . .	3:4220
	2,5-Dichlorohydroquinone . . . . .	3:4690
	2,6-Dichlorohydroquinone . . . . .	3:4600
$C_6H_3O_2Cl_3$	2,3,5-Trichlorohydroquinone . . . . .	3:4052
$C_6H_2O_2Cl_4$	Tetrachlorohydroquinone . . . . .	3:4941
$C_6H_2O_4Cl_2$	2,5-Dichloro-3,6-dihydroxybenzoquinone-1,4 . . . . .	3:4970

## c. Trihydric

$C_6H_3O_3Cl_3$	4,5,6-Trichloropyrogallol . . . . .	3:4782
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$C_6H_3O_4Cl_3$	3,5,6-Trichloro-2-hydroxyhydroquinone . . . . .	3:4444
Contd.	2,4,6-Trichlorophloroglucinol . . . . .	3:4030

## 2. Of binuclear phenols

## a. Monohydric

a<sub>1</sub> WITH UNCONDENSED RINGS

$C_{12}H_9OCl$	3-Chloro-2-hydroxybiphenyl . . . . .	3:1757
	5-Chloro-2-hydroxybiphenyl . . . . .	3:8980
	3-Chloro-4-hydroxybiphenyl . . . . .	3:1900
	4'-Chloro-4-hydroxybiphenyl . . . . .	3:4262

a<sub>2</sub> WITH CONDENSED RINGS

$C_{10}H_7OCl$	2-Chloronaphthol-1 . . . . .	3:1490
	3-Chloronaphthol-1 . . . . .	3:4170
	4-Chloronaphthol-1 . . . . .	3:3720
	5-Chloronaphthol-1 . . . . .	3:3960
	6-Chloronaphthol-1 . . . . .	3:2515
	7-Chloronaphthol-1 . . . . .	3:3810
	8-Chloronaphthol-1 . . . . .	3:1610
$C_{10}H_6OCl_2$	2,3-Dichloronaphthol-1 . . . . .	3:2935
	2,4-Dichloronaphthol-1 . . . . .	3:3250
	5,7-Dichloronaphthol-1 . . . . .	3:3985
	5,8-Dichloronaphthol-1 . . . . .	3:3420
	6,7-Dichloronaphthol-1 . . . . .	3:4315
	7,8-Dichloronaphthol-1 . . . . .	3:2635
$C_{10}H_7OCl$	1-Chloronaphthol-2 . . . . .	3:1700
	3-Chloronaphthol-2 . . . . .	3:2545
	4-Chloronaphthol-2 . . . . .	3:3045
	5-Chloronaphthol-2 . . . . .	3:3945
	6-Chloronaphthol-2 . . . . .	3:3500
	7-Chloronaphthol-2 . . . . .	3:3925
	8-Chloronaphthol-2 . . . . .	3:2965
$C_{10}H_6OCl_2$	1,3-Dichloronaphthol-2 . . . . .	3:1990
	1,4-Dichloronaphthol-2 . . . . .	3:3840
	1,6-Dichloronaphthol-2 . . . . .	3:3600
	3,4-Dichloronaphthol-2 . . . . .	3:3295
	4,8-Dichloronaphthol-2 . . . . .	3:4420
	5,8-Dichloronaphthol-2 . . . . .	3:4155

$C_7H_4O_2Cl_2$	2,6-Dichloro-3-hydroxybenzaldehyde. . . . .	3:4160
Contd.	4,6-Dichloro-3-hydroxybenzaldehyde. . . . .	3:3952
	3,5-Dichloro-4-hydroxybenzaldehyde. . . . .	3:4400
$C_7H_3O_2Cl_3$	2,4,6-Trichloro-3-hydroxybenzaldehyde. . . . .	3:3520

## B. Of Ketones

## 1. Dialkyl ketones

$C_3H_5OCl$	Chloroacetone. . . . .	3:5425
$C_3H_4OCl_2$	$\alpha,\alpha$ -Dichloroacetone. . . . .	3:5430
	$\alpha,\alpha'$ -Dichloroacetone. . . . .	3:0563
$C_3H_3OCl_3$	$\alpha,\alpha,\alpha$ -Trichloroacetone. . . . .	3:5620
	$\alpha,\alpha,\alpha'$ -Trichloroacetone. . . . .	3:5957
$C_3H_2OCl_4$	$\alpha,\alpha,\alpha,\alpha'$ -Tetrachloroacetone. . . . .	3:6035
	$\alpha,\alpha,\alpha',\alpha'$ -Tetrachloroacetone. . . . .	3:6050
$C_5H_7OCl_3$	Pentachloroacetone. . . . .	3:6205
$C_7OCl_4$	Hexachloroacetone. . . . .	3:6312
$C_4H_7OCl$	1-Chlorobutanone-2. . . . .	3:8012
	3-Chlorobutanone-2. . . . .	3:7593
	4-Chlorobutanone-2. . . . .	3:7640
$C_4H_6OCl_2$	1,3-Dichlorobutanone-2. . . . .	3:5900
$C_5H_5OCl$	1-Chloropentanone-2. . . . .	3:8217
	3-Chloropentanone-2. . . . .	3:7893
	4-Chloropentanone-2. . . . .	3:8243
	5-Chloropentanone-2. . . . .	3:9267
	1-Chloropentanone-3. . . . .	3:9268
	2-Chloropentanone-3. . . . .	3:7935
	1-Chloro-2-methylbutanone-3. . . . .	3:0269
	2-Chloro-2-methylbutanone-3. . . . .	3:7597
2. Alicyclic ketones		
$C_6H_8OCl$	2-Chlorocyclohexanone-1. . . . .	3:0120
	3-Chlorocyclohexanone-1. . . . .	3:9360
	4-Chlorocyclohexanone-1. . . . .	3:9364

$C_8OCl_2$	Hexachlorocyclohexadien-2,5-one-1 ("Hexachlorophenol") . . . . .	3:3180
$C_8O_2Cl_2$	1,2,3,4,6,6-Hexachlorocyclohexen-1-dione-3,5 ("Hexachlororesorcinol") . . . . .	3:3470
	2,3,5,5,6,6-Hexachlorocyclohexen-2-dione-1,4. . . . .	3:2360

## 3. Alkyl aryl ketones

## a. With chlorine only in alkyl

$C_8H_7OCl$	$\omega$ -Chloroacetophenone. . . . .	3:1212
$C_8H_6OCl_2$	$\omega,\omega$ -Dichloroacetophenone. . . . .	3:6835
$C_8H_5OCl_3$	$\omega,\omega,\omega$ -Trichloroacetophenone. . . . .	3:6847
$C_9H_7OCl$	$\alpha$ -Chloroethyl phenyl ketone. . . . .	3:0664
	$\beta$ -Chloroethyl phenyl ketone. . . . .	3:1115
	$\omega$ -Chloro- $\alpha$ -methylacetophenone. . . . .	3:9660
	$\omega$ -Chloro- $p$ -methylacetophenone. . . . .	3:1130
$C_{10}H_{11}OCl$	$\omega$ -Chloro-2,4-dimethylacetophenone. . . . .	3:1355
	$\omega$ -Chloro-2,5-dimethylacetophenone. . . . .	3:0245
	$\omega$ -Chloro-3,4-dimethylacetophenone. . . . .	3:1775
$C_{10}H_{10}OCl$	$p$ -Phenylphenacyl chloride. . . . .	3:3931
	$\alpha$ -Chlorobenzyl phenyl ketone. . . . .	3:1618

## b. With chlorine both in alkyl and aryl

$C_{10}H_9OCl_2$	$p$ -Chlorophenacyl chloride. . . . .	3:2990
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## c. With chlorine only in aryl

$C_8H_7OCl$	$o$ -Chloroacetophenone. . . . .	3:6615
	$m$ -Chloroacetophenone. . . . .	3:6315
	$p$ -Chloroacetophenone. . . . .	3:6735
$C_8H_5OCl$	$p$ -Chlorophenyl ethyl ketone. . . . .	3:0340

## 4. Diaryl ketones

$C_{12}H_9OCl$	2-Chlorobenzophenone. . . . .	3:0715
	3-Chlorobenzophenone. . . . .	3:2160
	4-Chlorobenzophenone. . . . .	3:1914

## b. Unsaturated

$C_3H_3OCl$   $\alpha$ -Chloroacrolein..... 3:9031

$C_4H_5OCl$   $\alpha$ -Chlorocrotonaldehyde..... 3:8117

## c. Relatives of the above

c<sub>1</sub> HYDRATES

$C_2H_4O_2Cl_2$  Dichloroacetaldehyde hydrate. . . . . 3:1085

$C_2H_3O_2Cl_2$  Chloral hydrate. . . . . 3:1270

$C_4H_7O_2Cl_3$  Butyrehloral hydrate. . . . . 3:1905

c<sub>2</sub> HEMIACETALS

$C_4H_8O_2Cl_2$  Dichloroacetaldehyde ethyl alcoholate.... 3:5310

$C_4H_7O_2Cl_2$  Chloral ethyl alcoholate. . . . . 3:0860

$C_6H_{11}O_2Cl_3$  Chloral *n*-butylalcoholate..... 3:0843

c<sub>3</sub> DIETHYLACETALS

$C_6H_{13}O_2Cl_2$  Chloroacetaldehyde diethylacetal..... 3:8223

$C_6H_{13}O_2Cl_2$  Dichloroacetaldehyde diethylacetal. . . . 3:6110

$C_6H_{11}O_2Cl_3$  Chloral diethylacetal. . . . . 3:6317

$C_7H_{15}O_2Cl$   $\beta$ -Chloropropionaldehyde diethylacetal.. 3:9490

$C_6H_{17}O_2Cl$   $\beta$ -Chloro-*n*-butyraldehyde diethylacetal 3:9594

c<sub>4</sub> ACETALS WITH CHLORINE ONLY IN ALCOHOL RADICALS

$C_6H_{12}O_2Cl_2$  Formaldehyde  $\beta,\beta'$ -dichloroisopropylethyl-acetal . . . . . 3:9394  
Acetaldehyde bis-( $\beta$ -chloroethyl)acetal.. 3:6210

c<sub>5</sub> POLYMERS

$C_6H_9O_2Cl_3$  Parachloroacetaldehyde..... 3:2300

$C_{12}H_{21}O_2Cl_2$  Para- $\beta$ -chloro-*n*-butyraldehyde..... 3:2650

Para- $\alpha$ -chloro-*n*-butyraldehyde..... 3:3220

## 2. Aromatic aldehydes

## a. Simple aldehydes

$C_7H_7OCl$  *o*-Chlorobenzaldehyde 3:6410

*m*-Chlorobenzaldehyde 3:6475

*p*-Chlorobenzaldehyde 3:0765

$C_7H_4OCl_2$  2,3-Dichlorobenzaldehyde..... 3:1480

2,4-Dichlorobenzaldehyde..... 3:1800

2,5-Dichlorobenzaldehyde . . . . . 3:1145

2,6-Dichlorobenzaldehyde . . . . . 3:1690

3,4-Dichlorobenzaldehyde . . . . . 3:0550

3,5-Dichlorobenzaldehyde... . . . . 3:1475

$C_7H_5OCl_3$  2,3,4-Trichlorobenzaldehyde. . . . . 3:2445

2,3,5-Trichlorobenzaldehyde. . . . . 3:1060

2,3,6-Trichlorobenzaldehyde.. . . . 3:2287

2,4,5-Trichlorobenzaldehyde . . . . . 3:3375

2,4,6-Trichlorobenzaldehyde . . . . . 3:1200

3,4,5-Trichlorobenzaldehyde . . . . . 3:2440

$C_7H_2OCl_4$  2,3,4,5-Tetrachlorobenzaldehyde.. . 3:3140

2,3,4,6-Tetrachlorobenzaldehyde..... 3:2700

2,3,5,6-Tetrachlorobenzaldehyde..... 3:2700

$C_7HOCl_5$  Pentachlorobenzaldehyde . . . . . 3:4892

## b. Phenolic aldehydes

$C_7H_5O_2Cl$  3-Chloro-2-hydroxybenzaldehyde..... 3:1010

4-Chloro-2-hydroxybenzaldehyde..... 3:0960

5-Chloro-2-hydroxybenzaldehyde. . . . . 3:2800

2-Chloro-3-hydroxybenzaldehyde..... 3:4085

4-Chloro-3-hydroxybenzaldehyde..... 3:3780

6-Chloro-3-hydroxybenzaldehyde..... 3:3350

2-Chloro-4-hydroxybenzaldehyde..... 3:4280

3-Chloro-4-hydroxybenzaldehyde..... 3:4065

$C_7H_4O_2Cl_2$  3,5-Dichloro-2-hydroxybenzaldehyde..... 3:2637

2,4-Dichloro-3-hydroxybenzaldehyde. . 3:4140

## B. OF ISOCYCLIC ACIDS.

## 1. With no other functional group.

a. Monobasic.

b. Dibasic.

c. Tribasic.

## 2. With some other functional group.

a. Phenolic acids.

b. Ether acids.

## C. ANHYDRIDES OF ACYCLIC ACIDS.

## 1. Saturated.

## 2. Unsaturated.

## D. ANHYDRIDES OF ISOCYCLIC ACIDS.

UNIT 6. CHLORO SUBSTITUTION PRODUCTS OF CARBOXYLIC ACIDS  
AND ANHYDRIDES

(For acyl chlorides see Unit 7)

## A. Of Acyclic Acids

## 1. With no other functional group

## a. Saturated monobasic

 $C_2H_3O_2Cl$  Chloroacetic acid..... 3:1370 $C_2H_3O_2Cl_2$  Dichloroacetic acid... 3:6208 $C_2HO_2Cl_3$  Trichloroacetic acid... 3:1150 $C_3H_5O_2Cl$   $\alpha$ -Chloropropionic acid 3:6125  
 $\beta$ -Chloropropionic acid 3:0160 $C_3H_4O_2Cl_2$   $\alpha,\alpha$ -Dichloropropionic acid..... 3:6162  
 $\alpha,\beta$ -Dichloropropionic acid.... 3:0855  
 $\beta,\beta$ -Dichloropropionic acid..... 3:1058 $C_3H_3O_2Cl_3$   $\alpha,\alpha,\beta$ -Trichloropropionic acid..... 3:1275 $C_3H_2O_2Cl_4$   $\alpha,\alpha,\beta,\beta$ -Tetrachloropropionic acid ..... 3:1850 $C_2HO_2Cl_5$  Pentachloropropionic acid..... 3:4895 $C_4H_7O_2Cl$   $\alpha$ -Chloro-*n*-butyric acid..... 3:9130  
 $\beta$ -Chloro-*n*-butyric acid..... 3:0035  
 $\gamma$ -Chloro-*n*-butyric acid..... 3:0020 $C_4H_6O_2Cl_2$   $\alpha,\beta$ -Dichloro-*n*-butyric acid  
Higher-melting isomer 3:1903  
Lower-melting isomer. 3:1375 $C_4H_3O_2Cl_3$   $\alpha,\alpha,\beta$ -Trichloro-*n*-butyric acid..... 3:1280 $C_4H_3O_2Cl_3$   $\alpha,\alpha,\gamma$ -Trichloro-*n*-butyric acid..... 3:1831  
Contd.  $\alpha,\beta,\beta$ -Trichloro-*n*-butyric acid..... 3:0925  
 $\gamma,\gamma,\gamma$ -Trichloro-*n*-butyric acid..... 3:1000 $C_4H_7O_2Cl$   $\alpha$ -Chloroisobutyric acid..... 3:0235  
 $\beta$ -Chloroisobutyric acid..... 3:0132 $C_5H_9O_2Cl$   $\alpha$ -Chloro-*n*-valeric acid 3:8783  
 $\beta$ -Chloro-*n*-valeric acid 3:0270  
 $\gamma$ -Chloro-*n*-valeric acid 3:9270  
 $\delta$ -Chloro-*n*-valeric acid 3:0075 $\alpha$ -Chloro- $\alpha$ -methyl-*n*-butyric acid ..... 3:8718  
 $\alpha$ -Chloro- $\beta$ -methyl-*n*-butyric acid..... 3:0050 $\beta$ -Chloro- $\alpha,\alpha$ -dimethylpropionic acid..... 3:0440

## b. Saturated dibasic

 $C_4H_4O_4Cl_2$  *dl*- $\alpha,\alpha'$ -Dichlorosuccinic acid..... 3:4711  
*meso*- $\alpha,\alpha'$ -Dichlorosuccinic acid..... 3:4930

## c. Unsaturated (olefinic) monobasic

 $C_3H_3O_2Cl$   $\alpha$ -Chloroacrylic acid.. 3:1445  
 $\beta$ -Chloroacrylic acid.. 3:2210 $C_3H_4O_2Cl_2$   $\alpha,\beta$ -Dichloroacrylic acid..... 3:2265  
 $\beta,\beta$ -Dichloroacrylic acid..... 3:1875 $C_4HO_2Cl_3$   $\alpha,\beta,\beta$ -Trichloroacrylic acid..... 3:1840





# CHAPTER IV

## DIVISION A. SOLIDS

(3:1000-3:1499)

3:1000  $\gamma,\gamma,\gamma$ -TRICHLORO-*n*-BUTYRIC ACID  $C_4H_5O_2Cl_3$  Beil. S.N. 162  
 $Cl_3C.CH_2.CH_2.COOH$

M.P. 55° (1)


Colorless ndls. from hot aq.

[For prepn. of  $\bar{C}$  from  $\gamma,\gamma,\gamma$ -trichloro-*n*-butyronitrile (see below) by hydrolysis with conc. HCl at 60° for 6 hrs. see (1).]

— $\gamma,\gamma,\gamma$ -Trichloro-*n*-butyronitrile: ndls. from pet. ether, m.p. 41° u.c.; b.p. 214-216° at 760 mm., 90-95° at 12 mm. (1). [From acrylonitrile with  $CHCl_3$  in pres. of aq. trimethylbenzylammonium hydroxide at 0.5° for 24 hrs. (11% yield (1)).] [Note that this nitrile upon acid hydrolysis gives  $\bar{C}$ , but upon alkaline hydrolysis gives succinic acid (1:0530), m.p. 188-189° (1).]

— $\gamma,\gamma,\gamma$ -Trichloro-*n*-butyramide: cryst. from toluene, m.p. 89-90° u.c. (1). [From  $\gamma,\gamma,\gamma$ -trichloro-*n*-butyronitrile (above) with 27%  $H_2O_2$  + aq. NaOH at 40-45° for 5 hrs. (1).]

3:1000 (1) Bruson, Niederhauser, Riener, Hester, *J. Am. Chem. Soc.* 67, 601 (1945).

3:1010 3-CHLORO-2-HYDROXYBENZALDE-  $C_7H_5O_2Cl$  Beil. VIII —  
 HYDE  VIII<sub>1</sub>-(523)  
 (3-Chlorosalicylaldehyde)

M.P. 55° (1)

54.5-55.5° (2)

54° (3) (4)

Long colorless ndls. from MeOH (1). — Readily sol. in usual org. solvents (1). — Volatile with steam [diff. from 3-chloro-4-hydroxybenzaldehyde (3:4065) (1)].

[For prepn. from *o*-chlorophenol (3:5980) with  $CHCl_3$  + alk. (10-15% yield (1)) or via condensation with formalin + alk. to 3-chloro-2-hydroxybenzyl alc. and oxidn. of latter with Na *m*-nitrobenzenesulfonate + alk. (2) see indic. refs.; from 3-chloro-2-hydroxybenzoic acid (3-chlorosalicylic ac.) (3:4745) by reductn. with Na/Hg in pres. of  $H_3BO_3$  see (4).]

$\bar{C}$  with satd. aq.  $NaHSO_3$  soln. yields  $NaHSO_3$  cpd. (1) (2).

$\bar{C}$  dissolves in aq. alk. with yel. color (4) (2).

$\bar{C}$  with aq.  $FeCl_3$  yields violet-red color (2).

$\bar{C}$  is not nitrated by cold  $AcOH/HNO_3$  soln. (1); but  $\bar{C}$  (2 g.) in  $AcOH$  (10 ml.) treated at 45° for 15 min. with soln. of 0.8 ml. conc.  $HNO_3$  ( $D = 1.42$ ) in  $AcOH$  (4 ml.), then poured into aq., gives (1) 2.15 g. 3-chloro-5-nitro-2-hydroxybenzaldehyde, yel. ndls. from dil. alc., m.p. 129° (1).

The methyl ether of  $\bar{C}$ , viz., 3-chloro-2-methoxybenzaldehyde, is a liq., h.p. abt. 255°, f.p. 0° (1).

$C_4H_5O_2Cl$	$\alpha$ -Chlorocrotonic acid.	3:2760
	$\alpha$ -Chloroisocrotonic acid. ....	3:1615
	$\beta$ -Chlorocrotonic acid.	3:2625
	$\beta$ -Chloroisocrotonic acid. ....	3:1300
	$\gamma$ -Chlorocrotonic acid.	3:2170

## d. Unsaturated (olefinic) dibasic

$C_4H_3O_4Cl$	Chlorofumaric acid. ...	3:4853
	Chloromaleic acid. ...	3:3432

$C_4H_2O_4Cl_2$	Dichloromaleic acid ..	3:3634
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## e. Unsaturated (acetylenic) monobasic

$C_3HO_2Cl$	Chloropropiolic acid..	3:1685
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## 2. With some other functional group

## a. Hydroxy monobasic

$C_4H_5O_3Cl_2$	$\beta,\beta$ -Dichloro- $\alpha$ -hydroxy-isobutyric acid .	3:2145
	$\beta,\beta'$ -Dichloro- $\alpha$ -hydroxy-isobutyric acid. .	3:2565

## B. Of Isocyclic Acids

## 1. With no other functional group

## a. Monobasic

$C_7H_5O_2Cl$	<i>o</i> -Chlorobenzoic acid	3:4150
	<i>m</i> -Chlorobenzoic acid	3:4392
	<i>p</i> -Chlorobenzoic acid	3:4940

$C_7H_3O_4Cl_2$	2,3-Dichlorobenzoic acid. ....	3:4650
	2,4-Dichlorobenzoic acid. ....	3:4560
	2,5-Dichlorobenzoic acid. ....	3:4340
	2,6-Dichlorobenzoic acid. ....	3:4200
	3,4-Dichlorobenzoic acid. ....	3:4925
	3,5-Dichlorobenzoic acid. ....	3:4840

$C_7H_3O_4Cl_3$	2,3,4-Trichlorobenzoic acid. ....	3:4810
	2,3,5-Trichlorobenzoic acid. ....	3:4485
	2,3,6-Trichlorobenzoic acid. ....	3:4500
	2,4,5-Trichlorobenzoic acid. ....	3:4630
	2,4,6-Trichlorobenzoic acid. ....	3:4545
	3,4,5-Trichlorobenzoic acid. ....	3:4920

$C_7H_2O_4Cl_4$	2,3,4,5-Tetrachlorobenzoic acid. ....	3:4790
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$C_7HO_4Cl_5$	Pentachlorobenzoic acid. ....	3:4910
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$C_8H_7O_2Cl$	3-Chloro-2-methylbenzoic acid. ....	3:4435
	4-Chloro-2-methylbenzoic acid. ....	3:4700
	5-Chloro-2-methylbenzoic acid. ....	3:4670
	6-Chloro-2-methylbenzoic acid. ....	3:3275

	4-Chloro-3-methylbenzoic acid. ....	3:4915
	5-Chloro-3-methylbenzoic acid. ....	3:4715
	6-Chloro-3-methylbenzoic acid. ....	3:4615

	2-Chloro-4-methylbenzoic acid. ....	3:4355
	3-Chloro-4-methylbenzoic acid. ....	3:4900

	2-Chlorophenylacetic acid. ....	3:2640
	3-Chlorophenylacetic acid. ....	3:1910
	4-Chlorophenylacetic acid. ....	3:3135

$C_{14}H_{11}O_2Cl$	Diphenyl-chloroacetic acid. ....	3:3585
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$C_{14}H_9O_2Cl_2$	Di-( <i>p</i> -chlorophenyl)-acetic acid. ....	3:4612
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$C_8H_5O_2Cl$	<i>o</i> -Chlorophenylpropionic acid. ....	3:3956
	<i>m</i> -Chlorophenylpropionic acid. ....	3:4102
	<i>p</i> -Chlorophenylpropionic acid. ....	3:4265

$C_{11}H_7O_2Cl$	2-Chloronaphthoic acid-1. ....	3:4330
	4-Chloronaphthoic acid-1. ....	3:4936
	5-Chloronaphthoic acid-1. ....	3:4944
	6-Chloronaphthoic acid-1. ....	3:4845
	7-Chloronaphthoic acid-1. ....	3:4942
	8-Chloronaphthoic acid-1. ....	3:4680

	1-Chloronaphthoic acid-2. ....	3:4885
	3-Chloronaphthoic acid-2. ....	3:4982
	5-Chloronaphthoic acid-2. ....	3:4952
	8-Chloronaphthoic acid-2. ....	3:4948

## b. Dibasic

$C_8H_6O_4Cl$	3-Chlorophthalic acid.....	3:4820
	4-Chlorophthalic acid.....	3:4390

$C_8H_4O_4Cl_2$	3,4-Dichlorophthalic acid.....	3:4880
	3,5-Dichlorophthalic acid.....	3:4580
	3,6-Dichlorophthalic acid.....	3:4870
	4,5-Dichlorophthalic acid.....	3:4890

$C_8H_2O_4Cl_4$	Tetrachlorophthalic acid.....	3:4946
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$C_8H_5O_4Cl$	4-Chloroisophthalic acid.....	3:4980
	5-Chloroisophthalic acid.....	3:4960

$C_8H_4O_4Cl_2$	4,6-Dichloroisophthalic acid.....	3:4965
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$C_8H_5O_4Cl$	Chloroterephthalic acid.....	3:4995
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$C_8H_4O_4Cl_2$	2,5-Dichloroterephthalic acid.....	3:4985
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## c. Tribasic

$C_9H_6O_4Cl$	5-Chlorobenzenetricarboxylic acid-1,2,4	3:4855
	2-Chlorobenzenetricarboxylic acid-1,3,5	3:4975

## 2. With same other functional group

## a. Phenolic acids

$C_7H_5O_3Cl$	3-Chloro-2-hydroxybenzoic acid.....	3:4745
	4-Chloro-2-hydroxybenzoic acid.....	3:4908
	5-Chloro-2-hydroxybenzoic acid.....	3:4705
	6-Chloro-2-hydroxybenzoic acid.....	3:4610

$C_7H_4O_3Cl_2$	3,5-Dichloro-2-hydroxybenzoic acid.....	3:4935
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$C_7H_5O_4Cl$	2-Chloro-3-hydroxybenzoic acid.....	3:4395
	4-Chloro-3-hydroxybenzoic acid.....	3:4933
	6-Chloro-3-hydroxybenzoic acid.....	3:4720

$C_7H_5O_3Cl$	2-Chloro-4-hydroxybenzoic acid.....	3:4430
Contd.	3-Chloro-4-hydroxybenzoic acid.....	3:4675

$C_7H_4O_3Cl_2$	3,5-Dichloro-4-hydroxybenzoic acid.....	3:4950
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## b. Ether acids

$C_8H_7O_3Cl$	<i>o</i> -Chlorophenoxyacetic acid.....	3:4260
	<i>m</i> -Chlorophenoxyacetic acid.....	3:3325
	<i>p</i> -Chlorophenoxyacetic acid.....	3:4375

$C_8H_5O_3Cl_2$	2,4-Dichlorophenoxyacetic acid.....	3:4095
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$C_8H_5O_3Cl_3$	2,4,5-Trichlorophenoxyacetic acid.....	3:4335
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## C. Anhydrides of Acyclic Acids

## 1. Saturated

$C_4H_4O_3Cl_2$	Chloroacetic acid anhydride.....	3:0730
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$C_4H_2O_3Cl_4$	Dichloroacetic acid anhydride.....	3:6430
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$C_4O_3Cl_6$	Trichloroacetic acid anhydride.....	3:6575
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## 2. Unsaturated

$C_4HO_3Cl$	Chloromaleic anhydride.....	3:0280
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$C_4O_3Cl_2$	Dichloromaleic anhydride.....	3:3635
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## D. Anhydrides of Isocyclic Acids

$C_8H_5O_3Cl$	3-Chlorophthalic anhydride.....	3:3900
	4-Chlorophthalic anhydride.....	3:2725

$C_8H_2O_3Cl_2$	3,4-Dichlorophthalic anhydride.....	3:3695
	3,5-Dichlorophthalic anhydride.....	3:2375
	3,6-Dichlorophthalic anhydride.....	3:4860
	4,5-Dichlorophthalic anhydride.....	3:4830

$C_8O_3Cl_4$	Tetrachlorophthalic anhydride.....	3:4947
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## UNIT 7. ACYL CHLORIDES

(Summary of Classification of Unit 7)

## A. OF ACYCLIC ACIDS (R.CO.Cl).

## 1. The radical (R) contains no chlorine.

- a. Corresponding acid is saturated and monobasic.
- b. Corresponding acid is saturated and dibasic.
- c. Corresponding acid is unsaturated and monobasic.
- d. Corresponding acid is unsaturated and dibasic.
- e. Corresponding acid contains also other functional groups.
  - e<sub>1</sub> Ether/acyl chloride.
  - e<sub>2</sub> Ester/acyl chloride.
  - e<sub>3</sub> Keto/acyl chloride.

## 2. The radical (R) does contain chlorine.

- a. Corresponding acid is saturated and monobasic.
- b. Corresponding acid is saturated and dibasic.
- c. Corresponding acid is unsaturated and monobasic.
- d. Corresponding acid is unsaturated and dibasic.
- e. Corresponding acid contains other functional groups.

## B. OF ISOCTYLIC ACIDS.

## 1. The radical (R) contains no chlorine.

- a. Corresponding acid is monobasic.
  - a<sub>1</sub> With —COOH group attached to ring.
  - a<sub>2</sub> With —COOH group attached to saturated side chain.
  - a<sub>3</sub> With —COOH group attached to unsaturated side chain.
  - a<sub>4</sub> With —COOH group attached to ring containing another functional group.
- b. Corresponding acid is dibasic.

## 2. The radical (R) does contain chlorine.

- a. Corresponding acid is monobasic.

## C. OF HETEROCYCLIC ACIDS.

## 1. The radical (R) contains no chlorine.

- a. Corresponding acid is monobasic.

## UNIT 7. ACYL CHLORIDES

## A. OF ACYCLIC ACIDS (R.CO.OH)

## 1. The radical (R) contains no chlorine

- a. Corresponding acid is saturated and monobasic

C<sub>2</sub>H<sub>3</sub>OCl Acetyl chloride ..... 3:7065C<sub>3</sub>H<sub>5</sub>OCl Propionyl chloride.... 3:7170C<sub>4</sub>H<sub>7</sub>OCl *n*-Butyryl chloride ... 3:7370  
Isobutyryl chloride... 3:7270C<sub>5</sub>H<sub>9</sub>OCl *n*-Valeryl chloride.... 3:7740

*α*-Methyl-*n*-butyryl  
chloride..... 3:7603  
*β*-Methyl-*n*-butyryl  
chloride..... 3:7560

*α,α*-Dimethylpropionyl  
chloride..... 3:7450

C<sub>6</sub>H<sub>11</sub>OCl *n*-Caproyl chloride.... 3:8168

*α*-Methyl-*n*-valeryl  
chloride..... 3:8070

*β*-Methyl-*n*-valeryl  
chloride..... 3:8035

*γ*-Methyl-*n*-valeryl  
chloride..... 3:8090

*α*-Ethyl-*n*-butyryl  
chloride..... 3:7990

*α,α*-Dimethyl-*n*-  
butyryl chloride.... 3:7900

*α,β*-Dimethyl-*n*-  
butyryl chloride.... 3:7965

*β,β*-Dimethyl-*n*-  
butyryl chloride.... 3:7890

C<sub>7</sub>H<sub>13</sub>OCl *n*-Heptanoyl chloride . 3:8520

$C_7H_{11}OCl$ Contd.	$\alpha$ -Methyl- <i>n</i> -caproyl chloride.....	3:9452	$C_7H_{15}O_2Cl_2$	Pimelyl (di)chloride ..	3:9450
	$\beta$ -Methyl- <i>n</i> -caproyl chloride.....	3:8305	$C_8H_{17}O_2Cl_2$	Suberyl (di)chloride ..	3:9576
	$\gamma$ -Methyl- <i>n</i> -caproyl chloride.....	3:8355	$C_8H_{17}O_2Cl_2$	Azelayl (di)chloride...	3:9680
	$\delta$ -Methyl- <i>n</i> -caproyl chloride.....	3:8365	$C_{10}H_{19}O_2Cl_2$	Sebacyl (di)chloride ..	3:9780
	$\alpha$ -Ethyl- <i>n</i> -valeryl chloride.....	3:8235	c. Corresp. acid is unsaturated and monobasic		
	$\alpha,\alpha$ -Dimethyl- <i>n</i> -valeryl chloride.....	3:9456	$C_4H_7OCl$	Acrylyl chloride.....	3:7153
	$\alpha,\beta$ -Dimethyl- <i>n</i> -valeryl chloride.....	3:9458	$C_4H_7OCl$	$\alpha$ -Crotonoyl chloride	3:7693
	$\gamma,\gamma$ -Dimethyl- <i>n</i> -valeryl chloride.....	3:9460	$C_6H_7OCl$	<i>cis</i> - $\alpha$ -Methylcrotonoyl chloride.....	3:9240
	$\alpha$ -Ethyl- $\beta$ -methyl- <i>n</i> - butyryl chloride ...	3:0462	$C_{18}H_{35}OCl$	Elaidyl chloride.....	3:9950
	$\alpha,\alpha,\beta$ -Trimethyl- <i>n</i> - butyryl chloride....	3:8145		Oleyl chloride.....	3:9940
			d. Corresp. acid is unsaturated and dibasic		
			$C_4H_2O_2Cl_2$	Fumaryl (di)chloride .	3:5875
			e. Corresp. acid contains also other functional groups		
$C_8H_{17}OCl$	<i>n</i> -Octanoyl chloride...	3:8680	e <sub>1</sub> ETHER/ACYL CHLORIDE		
$C_9H_{19}OCl$	Pelargonyl chloride...	3:8765	$C_4H_9O_2Cl$	Methoxyacetyl chloride.....	3:5225
$C_{10}H_{21}OCl$	<i>n</i> -Decanoyl chloride ..	3:8800	$C_4H_7O_2Cl$	Ethoxyacetyl chloride	3:7745
$C_{11}H_{23}OCl$	<i>n</i> -Undecanoyl chloride	3:9800	$C_4H_4O_2Cl_2$	Diglycolyl (di)- chloride.....	3:9092
$C_{12}H_{25}OCl$	<i>n</i> -Lauroyl chloride. ..	3:9858	e <sub>2</sub> ESTER/ACYL CHLORIDE		
$C_{13}H_{27}OCl$	<i>n</i> -Tridecanoyl chloride	3:0860	(For esters of chloroformic acid see Unit 8)		
$C_{14}H_{29}OCl$	Myristoyl chloride....	3:0885	$C_4H_9O_2Cl$	Ethoxalyl chloride	3:5625
$C_{15}H_{31}OCl$	<i>n</i> -Pentadecanoyl chloride.....	3:9900		Carbomethoxyacetyl chloride	3:9098-A
$C_{16}H_{33}OCl$	Palmitoyl chloride....	3:0912	$C_5H_9O_2Cl$	$\beta$ -(Carbomethoxy)pro- pionyl chloride....	3:9247
$C_{17}H_{35}OCl$	Margaroyl chloride...	3:9925		Carbomethoxyacetyl chloride.....	3:9246
$C_{18}H_{37}OCl$	Stearoyl chloride.....	3:9960	$C_5H_9O_2Cl$	$\gamma$ -(Carbomethoxy)- <i>n</i> - butyryl chloride....	3:9373
b. Corresp. acid is saturated and di- basic			$C_{11}H_{19}O_2Cl$	(Carbomethoxy)- pelargonyl chlorido.	3:9792
$COCl_2$	Carbonyl (di)chloride (phosgene).....	3:5000	e <sub>3</sub> KETO/ACYL CHLORIDE		
$C_2O_2Cl_2$	Oxalyl (di)chloride ...	3:5060	$C_4H_5O_2Cl$	Acetoacetyl chlorido..	3:9098
$C_3H_5O_2Cl_2$	Malonyl (di)chloride..	3:0030	2. The radical (R) does contain chlorine		
$C_4H_4O_2Cl_2$	Succinyl (di)chloride..	3:6200	a. Corresp. acid is saturated and mono- basic		
$C_4H_6O_2Cl_2$	Glutaryl (di)chloride .	3:6500	$C_2H_3OCl_2$	Chloroacetyl chloride.	3:5235
$C_6H_9O_2Cl_2$	Adipyl (di)chloride...	3:9352	$C_2HOCl_2$	Dichloroacetyl chloride.....	3:5290



$C_8H_7O_2Cl$	3-Methoxybenzoyl	
Contd.	chloride.....	3:6797
	4-Methoxybenzoyl	
	chloride.....	3:6590
	Phenoxyacetyl	
	chloride.....	3:8790
$C_8H_5O_2Cl$	Piperonyloyl chloride.	3:1960
$C_{14}H_9O_2Cl$	<i>o</i> -Benzoylbenzoyl	
	chloride.....	3:9880
	b. Corresp. acid is dibasic	
$C_8H_4O_2Cl_2$	<i>sym.-o</i> -Phthalyl (di)-	
	chloride.....	3:6900
	<i>unsym.-o</i> -Phthalyl	
	(di)chloride.....	3:2395
	Isophthalyl (di)-	
	chloride.....	3:0520
	Terephthalyl (di)-	
	chloride. ....	3:2205

## 2. The radical (R) does contain chlorine

## a. Corresp. acid is monobasic

$C_7H_4OCl_2$	<i>o</i> -Chlorobenzoyl	
	chloride .....	3:6640
	<i>m</i> -Chlorobenzoyl	
	chloride.....	3:6590
	<i>p</i> -Chlorobenzoyl	
	chloride.....	3:6550
$C_7OCl_4$	Pentachlorobenzoyl	
	chloride.....	3:2295

$C_{14}H_{10}OCl_2$	$\alpha$ -Chloro-diphenyl-	
	acetyl chloride.....	3:0885

## C. Of Heterocyclic Acids

## 1. Where R contains no chlorine

## a. Corresp. acid is monobasic

$C_8H_5O_2Cl$	Furoyl chloride.....	3:8515
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## UNIT 8. CHLORO SUBSTITUTION PRODUCTS OF ETHERS AND OF ESTERS

## (Summary of Classification of Unit 8)

## A. ETHERS.

## 1. Completely acyclic saturated ethers.

## a. Monoethers.

- a<sub>1</sub> Derived from symmetrical ethers.
- a<sub>2</sub> Derived from unsymmetrical ethers.

## b. Diethers.

## c. Ethers containing also other functions.

- c<sub>1</sub> Ether/alcohols.
- c<sub>2</sub> Ether/esters.
- c<sub>3</sub> Ether/ester/alcohols.
- c<sub>4</sub> Ether/ester/acyl halides.

## 2. Completely acyclic unsaturated ethers.

## 3. Cyclic ethers.

## a. Non-aromatic.

- a<sub>1</sub> Monoethers.
- a<sub>2</sub> Diethers.

## b. Aromatic ethers (phenol ethers).

## c. Heterocyclic ethers.

## B. ESTERS.

## 1. Esters of aliphatic acids.

## a. Acids containing no chlorine.

- a<sub>1</sub> From acetic acid.
- a<sub>2</sub> From oxalic acid.
- a<sub>3</sub> From carbonic acid.

## b. Saturated monobasic acids containing chlorine.

- b<sub>1</sub> From chloroacetic acid.
- b<sub>2</sub> From dichloroacetic acid.
- b<sub>3</sub> From trichloroacetic acid.

- b<sub>4</sub> From chloropropionic acid.
- b<sub>5</sub> From chlorobutyric acids.
- b<sub>6</sub> From chlorovaleric acids.
- c. Saturated dibasic acids containing chlorine
- d. Unsaturated monobasic acids containing chlorine.
- e. Unsaturated dibasic acids containing chlorine.
- f. Esters of chloroformic acid.
- g. Esters of keto acids.
- 2. Esters of aromatic acids.
  - a. Acids containing no chlorine.
  - b. Acids containing chlorine.
- 3. Esters of inorganic acids.
- 4. Esters containing also other functional groups.
  - a. Ester/alcohols.
    - a<sub>1</sub> From acids containing no chlorine.
    - a<sub>2</sub> From acids containing chlorine.
  - b. Ester/acyl chlorides.
  - c. Ester/ethers.
  - d. Ester/ether/alcohols.
  - e. Ester/ether/acyl chlorides.

## UNIT 8. CHLORINE SUBSTITUTION PRODUCTS OF ETHERS AND ESTERS

## A. Ethers

## 1. Completely acyclic saturated ethers

## a. Monoethers

a<sub>1</sub> DERIVED FROM SYMMETRICAL ETHERS

C <sub>4</sub> H <sub>9</sub> OCl	Chloromethyl methyl ether.....	3:7085
C <sub>4</sub> H <sub>9</sub> OCl <sub>2</sub>	sym-Dichlorodimethyl ether....	3:5245
C <sub>6</sub> H <sub>13</sub> OCl	α-Chloroethyl ethyl ether.....	3:7305
	β-Chloroethyl ethyl ether.....	3:7463
C <sub>6</sub> H <sub>13</sub> OCl <sub>2</sub>	α,α'-Dichlorodiethyl ether ...	3:7595
	α,β-Dichlorodiethyl ether.....	3:5640
	α,β'-Dichlorodiethyl ether ...	3:9150
	β,β'-Dichlorodiethyl ether.....	3:6025
C <sub>8</sub> H <sub>17</sub> OCl <sub>2</sub>	Octachlorodiethyl ether....	3:0738
C <sub>10</sub> OCl <sub>10</sub>	Decachlorodiethyl ether.....	3:1676
C <sub>8</sub> H <sub>17</sub> OCl <sub>2</sub>	β,β'-Dichloro-di-n-propyl ether....	3:8610
	γ,γ'-Dichloro-di-n-propyl ether ..	3:8745

C<sub>6</sub>H<sub>13</sub>OCl<sub>2</sub> β,β'-Dichloro-di-isopropyl ether. .. 3:8605  
Contd.

a<sub>2</sub> DERIVED FROM UNSYMMETRICAL ETHERS

C <sub>4</sub> H <sub>9</sub> OCl	Ethyl chloromethyl ether ..	3:7195
	α-Chloroethyl methyl ether ..	3:7150
	β-Chloroethyl methyl ether....	3:7265
C <sub>6</sub> H <sub>13</sub> OCl	α-Chloroethyl n-propyl ether ..	3:7525
C <sub>8</sub> H <sub>17</sub> OCl	α-Chloroethyl n-butyl ether....	3:9396
C <sub>7</sub> H <sub>15</sub> OCl	α-Chloroethyl n-amyl ether.....	3:9480

## b. Diethers

C <sub>6</sub> H <sub>13</sub> O <sub>2</sub> Cl <sub>2</sub>	Ethylene glycol bis-(β-chloroethyl) ether.....	3:6655
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## c. Ethers containing also other functions.

c<sub>1</sub> ETHER/ALCOHOLS

C <sub>4</sub> H <sub>9</sub> O <sub>2</sub> Cl	β-Chloro-β'-hydroxy-diethyl ether ...	3:9185
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c<sub>2</sub> ETHER/ESTERS

C <sub>6</sub> H <sub>13</sub> O <sub>2</sub> Cl	β-Methoxyethyl chloroacetate.....	3:9285
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$C_6H_7O_3Cl_3$   $\beta$ -Methoxyethyl tri-chloroacetate..... 3:9250

**c<sub>3</sub> ETHER/ESTER/ALCOHOLS**

$C_6H_{11}O_4Cl$  Diethylene glycol mono(chloroacetate) 3:9390

$C_8H_{15}O_4Cl$  Triethylene glycol mono(chloroacetate) 3:9588

**c<sub>4</sub> ETHER/ESTER/ACYL HALIDES**

$C_4H_7O_3Cl$   $\beta$ -Methoxyethyl chloroformate..... 3:9140

$C_4H_9O_3Cl$   $\beta$ -Ethoxyethyl chloroformate..... 3:9280

**2. Completely acyclic unsaturated ethers**

$C_4H_7OCl$   $\beta$ -Chloroethyl vinyl ether..... 3:7464

$C_4H_8OCl_2$   $\alpha,\beta$ -Dichlorovinyl ethyl ether..... 3:5540

$C_4OCl_2$  Di-(trichlorovinyl) ether..... 3:6373

**3. Cyclic ethers**

**a. Non-aromatic**

**a<sub>1</sub> MONOETHERS**

$C_3H_5OCl$  3-Chloro-1,2-epoxypropane..... 3:5358

$C_3H_5OCl_2$  3,3,3-Trichloro-1,2-epoxypropane..... 3:5760

$C_4H_7OCl$  3-Chloro-2-methyl-1,2-epoxypropane.... 3:7657

**a<sub>2</sub> DIETHERS**

$C_6H_8O_2Cl_2$  2,3-Dichlorodioxane-1,4..... 3:9105

**b. Aromatic ethers (phenol ethers)**

$C_7H_7OCl$  o-Chloroanisole..... 3:6255

m-Chloroanisole..... 3:6195

p-Chloroanisole..... 3:6300

$\omega$ -Chloroanisole..... 3:9448

$C_8H_9OCl$  o-Chlorophenetole... 3:8735

m-Chlorophenetole... 3:6323

p-Chlorophenetole... 3:0090

$\omega$ -Chlorophenetole... 3:0165

$C_9H_{11}OCl$   $\gamma$ -Chloro-n-propyl phenyl ether..... 3:8820

$C_{13}H_{15}O_2Cl$   $\beta$ -Chloroethyl  $\beta'$ -phenoxyethyl ether. 3:0770

**c. Heterocyclic ethers**

$C_6H_9OCl$  Tetrahydro- $\alpha$ -furfuryl chloride.... 3:8152

**B. Esters**

Classified according to acid radicals; for classification according to alkyl or aryl radicals see Alphabetical Index.

**1. Esters of aliphatic acids**

**a. Acids containing no chlorine**

**b<sub>1</sub> FROM ACETIC ACID**

$C_3H_5O_2Cl$  Chloromethyl acetate. 3:5356

$C_4H_7O_2Cl$   $\alpha$ -Chloroethyl acetate. 3:7625

$\beta$ -Chloroethyl acetate. 3:5735

$C_4H_9O_2Cl$   $\beta$ -Chloro-n-propyl acetate..... 3:8180

$\gamma$ -Chloro-n-propyl acetate..... 3:8310

$C_6H_9O_2Cl_2$   $\beta,\gamma$ -Dichloro-n-propyl acetate.... 3:6220

$C_6H_7O_2Cl$   $\beta$ -Chloroisopropyl acetate..... 3:8150

$C_6H_9O_2Cl_2$   $\beta,\beta'$ -Dichloroisopropyl acetate..... 3:6318

$C_6H_9O_2Cl_3$   $\beta,\beta,\beta$ -Trichloro-*tert*-butyl acetate..... 3:6180

$C_7H_{11}O_4Cl_3$  3-Chloropropane-diol-1,2 diacetate... 3:6840

**a<sub>2</sub> FROM OXALIC ACID**

$C_6H_8O_4Cl_2$  bis-( $\beta$ -Chloroethyl) oxalate..... 3:0572

**a<sub>3</sub> FROM CARBONIC ACID**

$C_3O_2Cl_4$  bis-(Trichloromethyl) carbonate..... 3:1915

$C_6H_9O_3Cl_2$  Di-( $\beta$ -chloroethyl) carbonate..... 3:6790

$C_7H_{11}O_3Cl_2$  Di-( $\gamma$ -chloro-n-propyl) carbonate.. 3:6995

**b. Saturated monobasic acids containing chlorine**

**b<sub>1</sub> FROM CHLOROACETIC ACID**

$C_2H_5O_2Cl$  Methyl chloroacetate. 3:5585

$C_4H_7O_2Cl$  Ethyl chloroacetate... 3:5700

$C_6H_9O_2Cl_2$   $\beta$ -Chloroethyl chloroacetate..... 3:6230

$C_4H_7O_2Cl$   $\beta$ -Hydroxyethyl chloroacetate..... 3:6780

$C_5H_9O_2Cl$   $\beta$ -Methoxyethyl chloroacetate..... 3:9285

$C_6H_9O_2Cl$  *n*-Propyl chloroacetate  
Isopropyl chloroacetate..... 3:8160

$C_6H_{11}O_2Cl$  *n*-Butyl chloroacetate  
Isobutyl chloroacetate ..... 3:8375  
*sec*-Butyl chloroacetate..... 3:8350  
*ter*-Butyl chloroacetate..... 3:8220

$C_4H_7O_2Cl$  Ethylene glycol mono(chloroacetate).... 3:6780

$C_4H_7O_4Cl_2$  Ethylene glycol bis(chloroacetate) .... 3:0720

$C_4H_{11}O_4Cl$  Diethylene glycol mono(chloroacetate) 3:9390

$C_6H_{15}O_4Cl$  Triethylene glycol mono(chloroacetate) 3:9588

$C_6H_7O_2Cl$  Phenyl chloroacetate . 3:0565

$b_2$  FROM DICHLOROACETIC ACID

$C_3H_4O_2Cl_2$  Methyl dichloroacetate ..... 3:5655

$C_4H_6O_2Cl_2$  Ethyl dichloroacetate. 3:5850

$C_4H_6O_2Cl_2$   $\beta$ -Hydroxyethyl dichloroacetate ... 3:9107

$C_5H_9O_2Cl_2$  *n*-Propyl dichloroacetate ... 3:6000  
Isopropyl dichloroacetate. .... 3:5890

$b_3$  FROM TRICHLOROACETIC ACID

$C_3H_3O_2Cl_3$  Methyl trichloroacetate . . . . . 3:5900

$C_2O_2Cl_3$  Trichloromethyl trichloroacetate..... 3:0290

$C_4H_5O_2Cl_3$  Ethyl trichloroacetate ..... 3:5950

$C_4H_4O_2Cl_4$   $\beta$ -Chloroethyl tri-chloroacetate..... 3:6510

$C_4H_5O_3Cl_3$   $\beta$ -Hydroxyethyl tri-chloroacetate..... 3:9099

$C_4H_7O_2Cl_3$   $\beta$ -Methoxyethyl tri-chloroacetate..... 3:9250

$C_5H_9O_2Cl_3$  *n*-Propyl trichloroacetate . . . . . 3:0135  
Isopropyl trichloroacetate..... 3:5975

$C_6H_9O_2Cl_3$  *n*-Butyl trichloroacetate..... 3:6315  
Isobutyl trichloroacetate . . . . . 3:6140  
*sec*-Butyl trichloroacetate ..... 3:9372  
*ter*-Butyl trichloroacetate..... 3:0138

$C_7H_{11}O_2Cl_3$  *n*-Amyl trichloroacetate ..... 3:6560  
Isoamyl trichloroacetate ..... 3:6490  
*ter*-Amyl trichloroacetate ..... 3:6185

$b_4$  FROM CHLOROPROPIONIC ACIDS

$C_4H_7O_2Cl$  Methyl  $\alpha$ -chloropropionate..... 3:7908

$C_4H_7O_2Cl$  Ethyl  $\alpha$ -chloropropionate..... 3:8125

$C_4H_9O_2Cl$  *n*-Propyl  $\alpha$ -chloropropionate..... 3:9384  
Isopropyl  $\alpha$ -chloropropionate..... 3:8165

$C_5H_{11}O_2Cl$  *n*-Butyl  $\alpha$ -chloropropionate..... 3:8595  
Isobutyl  $\alpha$ -chloropropionate..... 3:9470

$C_6H_{13}O_2Cl$  Isoamyl  $\alpha$ -chloropropionate... 3:9580

$C_4H_7O_2Cl$  Methyl  $\beta$ -chloropropionate ..... 3:5765

$C_4H_7O_2Cl$  Ethyl  $\beta$ -chloropropionate ..... 3:8290

$C_5H_{11}O_2Cl$  *n*-Propyl  $\beta$ -chloropropionate ..... 3:8545  
Isopropyl  $\beta$ -chloropropionate..... 3:9388

$C_5H_{13}O_2Cl$  *n*-Butyl  $\beta$ -chloropropionate..... 3:9474  
Isobutyl  $\beta$ -chloropropionate ..... 3:8655

$C_6H_{15}O_2Cl$  Isoamyl  $\beta$ -chloropropionate..... 3:8730

$C_4H_5O_2Cl_2$	Methyl $\alpha,\beta$ -dichloro- propionate .....	3:9103	$C_6H_{12}O_4Cl_2$	Diethyl <i>d,l</i> - $\alpha,\alpha$ -di- chlorosuccinate.....	3:9578
$C_6H_9O_2Cl_2$	Ethyl $\alpha,\beta$ -dichloro- propionate .. . .	3:6090	$C_6H_8O_4Cl_2$	Dimethyl <i>meso</i> - $\alpha,\alpha$ -di- chlorosuccinate.....	3:0240
<i>b<sub>5</sub></i> FROM CHLOROBUTYRIC ACIDS					
$C_4H_7O_2Cl$	Methyl $\alpha$ -chloro- <i>n</i> - butyrate.....	3:8103	<i>d.</i> From unsaturated monobasic acids containing chlorine		
$C_6H_{11}O_2Cl$	Ethyl $\alpha$ -chloro- <i>n</i> - butyrate.....	3:8307	$C_6H_7O_2Cl$	Methyl $\alpha$ -chloro- acrylate.....	3:9096
$C_6H_9O_2Cl$	Methyl $\beta$ -chloro- <i>n</i> - butyrate .....	3:8224	$C_6H_7O_2Cl$	Ethyl $\alpha$ -chloro- acrylate .....	3:9242
$C_6H_{11}O_2Cl$	Ethyl $\beta$ -chloro- <i>n</i> - butyrate.....	3:8373	$C_6H_7O_2Cl$	Methyl $\alpha$ -chloro- crotonate.....	3:5870
$C_6H_9O_2Cl$	Methyl $\gamma$ -chloro- <i>n</i> - butyrate.....	3:8517	$C_6H_9O_2Cl$	Ethyl $\alpha$ -chloro- crotonate.....	3:8523
$C_6H_{11}O_2Cl$	Ethyl $\gamma$ -chloro- <i>n</i> - butyrate.....	3:8597	$C_6H_7O_2Cl$	Methyl $\beta$ -chloro- crotonate.....	3:9244
$C_6H_9O_2Cl$	Methyl $\alpha$ -chloroiso- butyrate.....	3:7918	$C_6H_9O_2Cl$	Ethyl $\beta$ -chloro- crotonate. ....	3:8538
$C_6H_{11}O_2Cl$	Ethyl $\alpha$ -chloroiso- butyrate.....	3:8147	$C_6H_8O_2Cl$	Ethyl $\gamma$ -chloro- crotonate.....	3:8657
$C_6H_9O_2Cl_3$	Ethyl $\alpha,\alpha,\beta$ -trichloro- <i>n</i> -butyrate....	3:6380	$C_6H_9O_2Cl$	Ethyl $\alpha$ -chloroiso- crotonate, .....	3:9368
<i>b<sub>6</sub></i> FROM CHLOROVALERIC ACIDS					
$C_6H_{11}O_2Cl$	Methyl $\alpha$ -chloro- <i>n</i> - valerate.....	3:8264	$C_6H_7O_2Cl$	Methyl $\beta$ -chloroiso- crotonate.....	3:8028
$C_7H_{13}O_2Cl$	Ethyl $\alpha$ -chloro- <i>n</i> - valerate .....	3:8596	$C_6H_9O_2Cl$	Ethyl $\beta$ -chloroiso- crotonate.....	3:8325
$C_7H_{13}O_2Cl$	Ethyl $\beta$ -chloro- <i>n</i> - valerate.....	3:8629	<i>e.</i> From unsaturated dibasic acids con- taining chlorine		
$C_7H_{13}O_2Cl$	Ethyl $\gamma$ -chloro- <i>n</i> - valerate .....	3:8703	$C_6H_7O_4Cl$	Dimethyl chloro- fumarate .....	3:6582
$C_7H_{13}O_2Cl$	Ethyl $\delta$ -chloro- <i>n</i> - valerate .. . . .	3:8727	$C_6H_{11}O_4Cl$	Diethyl chloro- fumarate .....	3:6864
$C_7H_{13}O_2Cl$	Ethyl $\alpha$ -chloro- $\alpha$ - methyl- <i>n</i> -butyrate	3:8518	$C_6H_7O_4Cl$	Dimethyl chloro- maleate.....	3:9351
	Ethyl $\alpha$ -chloro- $\beta$ - methyl- <i>n</i> -butyrate..	3:8528	$C_6H_{11}O_4Cl$	Diethyl chloro- maleate.....	3:6697
<i>c.</i> From saturated dibasic acids con- taining chlorine					
$C_6H_8O_2Cl_2$	Dimethyl <i>d,l</i> - $\alpha,\alpha$ - dichlorosuccinate...	3:0485	<i>f.</i> From chloroformic acid		
			$C_2H_3O_2Cl$	Methyl chloroformate	3:5075
			$C_2H_3O_2Cl_2$	Chloromethyl chloro- formate.. .....	3:5275
			$C_2HO_2Cl_2$	Dichloromethyl chloro- formate.....	3:5315

- @ 3-Chloro-2-hydroxybenzaldehyde: lfts. from dil. alc., m.p. 167-168° (2).  
 — 3-Chloro-2-hydroxybenzaldehyde phenylhydrazine: unrecorded.  
 — 3-Chloro-2-hydroxybenzaldehyde *p*-nitrophenylhydrazine: unrecorded.  
 — 3-Chloro-2-hydroxybenzaldehyde 2,4-dinitrophenylhydrazine: unrecorded.  
 @ 3-Chloro-2-hydroxybenzaldehyde semicarbazone: cryst. from 50% AcOH, m.p. 210-213° (2).

3:1010 (1) Davies, Rubinstein, *J. Chem. Soc.* 123, 2850 (1923). (2) Hanus, *J. prakt. Chem.* (2) 139, 263-264 (1911). (3) Duff, *J. Chem. Soc.* 1911, 547-550. (4) Bayer and Co., Ger. 228,839, Nov. 22, 1910; *Cent.* 1911, 1 51.

### 3:1020 4,6-DICHLORO-2-METHYLPHENOL

 $C_7H_6OCl_2$ 

Beil. VI - 359

 (4,6-Dichloro-*o*-cresol)

 VI<sub>1</sub>-(174)

 VI<sub>2</sub>-(332)


M.P. 56° (1)	B.P. 226.5° (1)
55° (2) (7)	131° at 28 mm. (5)
54-55° (3)	73-78° at 4 mm. (6)
54° u.c. (1)	
53-51° (5)	

Ndls. from hot aq. or pet. ether. Spar. sol. cold but more eas. sol. hot aq.; eas. sol. alc., ether,  $CHCl_3$ ,  $CS_2$ . Volatile with steam.

[For prepn. of  $\bar{C}$  from *o*-cresol (1.1400) with  $Cl_2$  (7) (1) in  $CCl_4$  (61% yield (2)) in  $CCl_4$  in pres. of  $I_2$  (8) or in pres. of  $PCl_5$  in sunlight at elevated temp. (8), with  $Cl_2$  in NaOH soln. at room temp. (5), or with  $SO_2Cl_2$  (3), see indic. refs.; for formn. from 2-methylphenolsulfonic acid-4,6 (6) in nitrobenzene with  $Cl_2$  (other products are also formed) see (6).]

[ $\bar{C}$  with dry  $NH_3$  gas at room temp. (9) forms a cpd.,  $\bar{C} \cdot 2NH_3$  (9);  $\bar{C}$  on evapn. of alc.  $NH_3$  soln. does not give an  $NH_3$  salt but is recovered unchanged (dif. from 2,6-dichloro-4-methylphenol (3:0400) q.v.) (7) ]

[ $\bar{C}$  (1 pt.) in 2 pts. ice-cold  $HNO_3$  ( $D = 1.45$ ) stood 24 hrs. gives (37% yield (2)) a prod. of compn.  $C_7H_4O_4N_2Cl_2$ , white ndls. from dry ether by pptn. with pet. ether, m.p. 109° dec. (2) ]

[ $\bar{C}$  with boilg. dil.  $HNO_3$  oxidizes (7) to oxalic acid (1.0115);  $\bar{C}$  on oxidn. with  $K_2Cr_2O_7$  + dil.  $H_2SO_4$  gives (4) 6-chloro-2-methylbenzoquinone-1,4 (6-chloro-*p*-toluquinone) [Boil. VII-650, VII<sub>1</sub>-(353)], yel ndls., vol. with steam, m.p. 90° (4);  $\bar{C}$  digested with aqua regia for 1½ hrs. at 100° gives (16% yield (5)) 3,5,6-trichloro-2-methylbenzoquinone-1,4 (trichloro-*p*-toluquinone) [Boil. VII-651, VII<sub>1</sub>-(351)], yel lfts. from alc., m.p. 231° (5);  $\bar{C}$  with  $CrO_3$ /AcOH gives a mixt. (1) of chlorinated quinones ]

[ $\bar{C}$  does not react with  $PCl_5$  (10);  $\bar{C}$  on monosulfonation with fuming  $H_2SO_4$  (65%  $SO_3$ ) at 50° yields (11) 4,6-dichloro-2-methylphenolsulfonic acid-3; for condensation of  $\bar{C}$  with benzaldehydesulfonic acid-1 and use as methylating agt. see (12) ]

[ $\bar{C}$  in MeOH/KOH refluxed 6½ hrs. with MeI (74% yield (1)), or  $\bar{C}$  in aq. alk. with  $MgSO_4$  (1) gives the corresp. methyl ether (4,6-dichloro-2-methylphenylether), m.p. 37° (1), 2-30° (3), b.p. 230° (1);  $\bar{C}$  in aq. alk. soln. treated with  $H_2SO_4$  gives (1) corresp. ethyl ether (4,6-dichloro-2-methylphenylether), m.p. 27.5° (1) ]

## d. Ester/ether/alcohols

- $C_6H_{11}O_4Cl$  Diethylene glycol  
mono(chloroacetate) **3:9390**
- $C_6H_{13}O_5Cl$  Triethylene glycol  
mono(chloroacetate) **3:9538**

## e. Ester/ether/acyl halides

- $C_6H_9O_3Cl$   $\beta$ -Methoxyethyl chloro-  
formate..... **3:9140**
- $C_6H_9O_3Cl$   $\beta$ -Ethoxyethyl chloro-  
formate..... **3:9280**

$C_2O_2Cl_4$	Trichloromethyl chloroformate ..	3:5515
$C_2H_5O_2Cl$	Ethyl chloroformate .	3:7295
$C_2H_5O_2Cl_2$	$\beta$ -Chloroethyl chloroformate.....	3:5780
$C_4H_7O_2Cl$	$\beta$ -Methoxyethyl chloroformate... ..	3:9140
$C_4H_9O_2Cl$	$\beta$ -Ethoxyethyl chloroformate.....	3:9280
$C_4H_7O_2Cl$	<i>n</i> -Propyl chloroformate. ....	3:7540
$C_6H_9O_2Cl_2$	$\gamma$ -Chloro- <i>n</i> -propyl chloroformate . . .	3:6010
$C_4H_7O_2Cl$	Isopropyl chloroformate . . . .	3:7405
$C_6H_9O_2Cl$	<i>n</i> -Butyl chloroformate . . . .	3:7980
	Isobutyl chloroformate. ....	3:7760
$C_7H_{11}O_2Cl$	<i>n</i> -Amyl chloroformate	3:9350
	Isoamyl chloroformate	3:8215
$C_4H_9O_2Cl$	Allyl chloroformate	3:7487
	Isopropenyl chloroformate. ....	3:7358
$C_7H_{11}O_2Cl$	Cyclohexyl chloroformate. ..	3:6770
$C_6H_7O_2Cl$	Benzyl chloroformate.	3:9565
<i>g. Keto acids</i>		
$C_4H_9O_2Cl$	Ethyl $\alpha$ -chloroacetoacetate .	3:6207
	Ethyl $\gamma$ -chloroacetoacetate. ....	3:6375
<b>2. Esters of aromatic acids</b>		
<i>a. From acids containing no chlorine</i>		
$C_8H_5O_2Cl$	$\beta$ -Chloroethyl benzoate	3:8860
<i>b. From acids containing chlorine</i>		
$C_9H_7O_2Cl$	Methyl <i>o</i> -chlorobenzoate..	3:6695
$C_9H_9O_2Cl$	Ethyl <i>o</i> -chlorobenzoate.....	3:6800
$C_9H_7O_2Cl$	Methyl <i>m</i> -chlorobenzoate..	3:6670
$C_9H_9O_2Cl$	Ethyl <i>m</i> -chlorobenzoate... .	3:6770

$C_8H_7O_2Cl$	Methyl <i>p</i> -chlorobenzoate.....	3:0535
$C_9H_9O_2Cl$	Ethyl <i>p</i> -chlorobenzoate.....	3:6750
<b>3. Esters of inorganic acids</b>		
$C_2H_5OCl$	Ethyl hypochlorite....	3:7022
$C_4H_9OCl$	<i>ter</i> -Butyl hypochlorite	3:7165
$C_5H_{11}OCl$	<i>ter</i> -Amyl hypochlorite.	3:0287
<b>4. Esters containing also other functional groups</b>		
<i>a. Ester/alcohols</i>		
<i>a<sub>1</sub> FROM ACIDS WITH NO CHLORINE</i>		
$C_6H_9O_2Cl$	$\beta$ -Chloro- $\alpha$ -hydroxy- <i>n</i> -propyl acetate ..	3:6775
	$\alpha$ -Chloro- $\beta$ -hydroxy- <i>n</i> -propyl acetate....	3:6648
	$\beta$ -Chloro- $\beta'$ -hydroxyisopropyl acetate. .	3:6517
<i>a<sub>2</sub> FROM ACIDS CONTAINING CHLORINE</i>		
$C_4H_7O_2Cl$	$\beta$ -Hydroxyethyl chloroacetate. . . . .	3:6780
$C_4H_9O_2Cl_2$	$\beta$ -Hydroxyethyl dichloroacetate.....	3:9107
$C_4H_9O_2Cl_3$	$\beta$ -Hydroxyethyl trichloroacetate.....	3:9099
<i>b. Ester/acyl halides</i>		
$C_2H_5O_2Cl$	Ethoxalyl chloride....	3:5625
	Carbomethoxyacetyl chloride . . . .	3:9098-A
$C_4H_7O_2Cl$	$\beta$ -(Carbomethoxy)propionyl chloride.....	3:9247
	Carbomethoxyacetyl chloride. ....	3:9240
$C_6H_9O_2Cl$	$\gamma$ -(Carbomethoxy)- <i>n</i> -butyryl chloride....	3:9373
$C_{11}H_{19}O_2Cl$	$\omega$ -(Carbomethoxy)-pelargonyl chloride .	3:0792
<i>c. Ester/ethers</i>		
$C_4H_9O_2Cl$	$\beta$ -Methoxyethyl chloroacetate.....	3:9285
$C_6H_7O_2Cl_2$	$\beta$ -Methoxyethyl trichloroacetate.....	3:9250
$C_2H_5O_2Cl_2$	Chloralide.....	3:3510

- 3:7151** 4-Chlorohutene-1  
**3:7205** 1-Chlorobutene-2  
**3:7105** 2-Chlorohutene-2  
**3:8117** 2-Chlorobuten-2-ol-1  
**3:1615** *cis*-2-Chlorobuten-2-ol-1  
**3:2760** *trans*-2-Chlorobuten-2-ol-1  
**3:1300** *cis*-3-Chlorobuten-2-ol-1  
**3:2625** *trans*-3-Chlorobuten-2-ol-1  
**3:2170** 4-Chlorobuten-2-ol-1  
**3:8240** 2-Chlorobuten-2-ol-1  
**3:8270** 3-Chlorobuten-2-ol-1  
**3:9114** 4-Chlorobuten-2-ol-1  
**3:9113** 2-Chlorobuten-3-ol-1  
**3:8110** 1-Chlorobuten-3-ol-2  
**3:9115** 3-Chlorobuten-3-ol-2  
**3:9114** 1-Chlorobuten-2-ol-4  
**3:8270** 2-Chlorobuten-2-ol-4  
**3:7070** 1-Chlorobuten-3-yn-1  
**3:9160**  $\beta$ -Chloro-*n*-butyl alcohol  
**3:9165**  $\gamma$ -Chloro-*n*-butyl alcohol  
**3:9170**  $\delta$ -Chloro-*n*-butyl alcohol  
**3:7752** Chloro-*ter*-butyl alcohol  
**3:8780** ( $\beta$ -Chloro-*ter*-butyl)benzene  
**3:7090**  $\gamma$ -Chloro- $\alpha$ -butylene  
**3:7205**  $\alpha$ -Chloro- $\beta$ -butylene  
**3:8830** 2-Chloro-4-*n*-butylphenol  
**3:9760** 2-Chloro-4-*ter*-butylphenol  
**3:7175** 1-Chlorobutyn-2  
**3:9594**  $\beta$ -Chlorobutyral  
**3:9109**  $\alpha$ -Chloro-*n*-butyraldehyde  
**3:0110**  $\beta$ -Chloro-*n*-butyraldehyde  
**3:9111**  $\gamma$ -Chloro-*n*-butyraldehyde  
**3:0594**  $\delta$ -Chloro-*n*-butyraldehyde  
**3:9130** diethylacetal  
**3:0035**  $\alpha$ -Chloro-*n*-butyric acid  
**3:0020**  $\beta$ -Chloro-*n*-butyric acid  
**3:5570**  $\gamma$ -Chloro-*n*-butyric acid  
**3:9100**  $\alpha$ -Chloro-*n*-butyryl chloride  
**3:5970**  $\beta$ -Chloro-*n*-butyryl chloride  
**3:0180**  $\gamma$ -Chloro-*n*-butyryl chloride  
**3:0745** *p*-(5)-Chlorocavacrol  
**3:2470** 3-Chlorocatechol  
**3:9195** 4-Chlorocatechol  
**3:9206** 1-Chloro-2-(chloromethyl)-  
butadiene-1,3  
**3:9534** 3-Chloro-2-(chloromethyl)-  
butene-1  
**3:6633** 4-Chloro-3-(chloromethyl)-  
heptane  
**3:5633** 3-Chloro-2-(chloromethyl)-  
propene-1  
**3:1430** 1-Chloro-2-(chloromethyl)-  
propene-2  
**3:2280** 1-Chloro-2,2-*bis*-(*p*-chlorophenyl)-  
ethylene  
**3:0780** 3-Chloro-*o*-cresol  
**3:1815** 4-Chloro-*o*-cresol  
**3:8615** 5-Chloro-*o*-cresol  
**3:1055** 6-Chloro-*o*-cresol  
**3:1535** 2-Chloro-*m*-cresol  
**3:0700** 4-Chloro-*m*-cresol  
**3:6215** 6-Chloro-*m*-cresol  
**3:1025** 2-Chloro-*p*-cresol  
**3:8117** 3-Chloro-*p*-cresol  
**3:1615**  $\alpha$ -Chlorocrotonaldehyde  
**3:2760** *allo*- $\alpha$ -Chlorocrotonic acid  
**3:2625**  $\alpha$ -Chlorocrotonic acid  
**3:2170**  $\beta$ -Chlorocrotonic acid  
**3:8240**  $\gamma$ -Chlorocrotonic acid  
**3:8270**  $\beta$ -Chlorocrotonyl alcohol  
**3:8705**  $\gamma$ -Chlorocrotonyl alcohol  
**3:8040** *p*-Chlorocumene  
**3:9374** Chlorocyclohexane  
**3:0175** *cis*-2-Chlorocyclohexanol-1  
**3:9376** *trans*-2-Chlorocyclohexanol-1  
**3:0120** 4-Chlorocyclohexanol-1  
**3:9360** 2-Chlorocyclohexanone-1  
**3:9364** 3-Chlorocyclohexanone-1  
**3:7545** 4-Chlorocyclohexanone-1  
**3:8775** Chlorocyclopentane  
**3:8770** 2-Chloro-*p*-cymene  
**3:8785** 3-Chloro-*p*-cymene  
**3:0014** 1-Chlorodecane  
**3:9712** 10-Chlorodecanol-1  
**3:0014** 5-Chlorodecene-5  
**3:1618**  $\omega$ -Chloro-*n*-decyl alcohol  
**3:1618**  $\alpha$ -Chlorodesoxybenzoin  
**3:7305** *ms*-Chlorodesoxybenzoin  
**3:9716**  $\alpha$ -Chlorodiethyl ether  
**3:7035** 4-Chloro-3,4-dimethylhexene-2  
**3:1355**  $\alpha$ -Chlorodiethylketone  
**3:1775**  $\omega$ -Chloro-2,4-dimethylaceto-  
phenone  
**3:0245**  $\omega$ -Chloro-3,4-dimethylaceto-  
phenone  
**3:8645**  $\omega$ -Chloro-2,5-dimethylaceto-  
phenone  
**3:8675** 3-Chloro-1,2-dimethylbenzene  
**3:8590** 4-Chloro-1,2-dimethylbenzene  
**3:8665** 2-Chloro-1,3-dimethylbenzene  
**3:8640** 4-Chloro-1,3-dimethylbenzene  
**3:7590** 5-Chloro-1,3-dimethylbenzene  
**3:7475** 2-Chloro-1,4-dimethylbenzene  
**3:7555** 1-Chloro-2,2-dimethylbutane  
**3:7600** 3-Chloro-2,2-dimethylbutane  
**3:7340** 4-Chloro-2,2-dimethylbutane  
**3:7520** 2-Chloro-2,3-dimethylbutane  
**3:7340** 2-Chloro-3,3-dimethylbutene-1  
**3:7035** 1-Chloro-2,3-dimethylbutene-2  
**3:8780** 3-Chloro-2,2-dimethylbutene-3  
**3:9656** Chlorodimethyl ether  
**3:9650** ( $\beta$ -Chloro- $\alpha$ , $\alpha$ -dimethyl)ethyl-  
benzene  
**3:9632** 3-Chloro-2,2-dimethyl-3-ethyl-  
pentane  
**3:9630** 3-Chloro-2,3-dimethylheptane  
**3:9554** 5-Chloro-2,5-dimethylheptane  
**3:9556** 4-Chloro-3,6-dimethylheptene-2  
**3:9529** 3-Chloro-2,3-dimethylhexane  
**3:9528** 2-Chloro-2,5-dimethylhexane  
**3:9527** 2-Chloro-3,4-dimethylhexane  
**3:9528** 4-Chloro-2,5-dimethylhexene-2  
**3:9738** 4-Chloro-3,5-dimethylhexene-2  
**3:9738** 2-Chloro-2,5-dimethylhexene-3  
**3:9738** 3-Chloro-2,4-dimethylhexene-4  
**3:9738** 3-Chloro-2,3-dimethyloctane

## V. ALPHABETICAL NAME INDEX TO COMPOUNDS OF ORDER 3

1. Note that this index refers only to numbered compounds of Order 3; for practical reasons it cannot include the large number of related products which are incidentally mentioned within the text of these numbered individuals.

2. In this alphabetical name index all literal prefixes (such as those below) are ignored in establishing the alphabetical sequence. Note, however, that "iso" is not recognized as a prefix but is construed as an integral part of the name and therefore indexed under the letter I.

3. Within any given group of related prefixes the following sequences are employed:

*d,l*- . . . *allo*- . . . *meso*-  
*erythro*- . . . *threo*-  
*cis*- . . . *trans*-  
*prim.*- . . . *sec.*- . . . *ter*-  
*sym.*- . . . *unsym.*-

*h*-*m*. . . *l*-*m*.  
*o*- . . . *m*- . . . *p*-  
 $\alpha$ - . . .  $\beta$ - . . .  $\gamma$ - . . .  $\delta$ - . . .  $\omega$ -  
*bis*- . . . *tris*-  
solid . . . liquid

4. Note that except when needed to distinguish from other stereoisomers the prefix *d,l* is omitted from the alphabetical index names even when included in text of the individual compound.

5. Whenever in a particular name the syllable (di) is inserted in parentheses to avoid possible ambiguity, such syllable is ignored in establishing the alphabetical sequence.

6. For a given family of derivatives of the same halogen-free parent, the sequence of listing is based upon the parent, e.g., all the dichloro substitution products of naphthol-1 precede all those derived from naphthol-2.

A			
3:6210	Acetaldehyde <i>bis</i> -( $\beta$ -chloroethyl)-acetal	3:8150	2-Acetoxy-1-chloropropano
3:9098	Acetoacetyl chloride	3:8160	1-Acetoxy-2-chloropropano
3:6317	$\beta$ -Aceto- $\alpha$ -chlorohydrin	3:8310	1-Acetoxy-3-chloropropano
3:6775	$\gamma$ -Aceto- $\alpha$ -chlorohydrin	3:7065	Acetyl chloride
3:6618	$\alpha$ -Aceto- $\beta$ -chlorohydrin	3:5012	<i>cis</i> -Acetyleno dichloride
3:6720	$\gamma$ -Aceto- $\alpha,\beta$ -dichlorohydrin	3:5028	<i>trans</i> -Acetyleno dichloride
3:6318	$\beta$ -Aceto- $\alpha,\gamma$ -dichlorohydrin	3:5030	Acetylene dichloride (ordinary mixt.)
3:7140	"Acetone (di)chloride"	3:5750	Acetylene tetrachloride
3:2662	Acetone chloroform	3:5555	Acetylidene tetrachloride
3:6180	"Acetone chloroform" acetate	3:9034	Acrolein dichloride
3:5425	Acetonyl chloride	3:5140	"Acrolein dichloride"
		3:5576	Acrolein hydrochloride



3:0015	1-Chlorohexadecane	3:4950	4-Chloroisophthalic acid
3:0525	16-Chlorohexadecanol-1	3:4960	5-Chloroisophthalic acid
3:0525	$\omega$ -Chloro- <i>n</i> -hexadecyl alcohol	3:7290	" $\beta$ -Chloroisoprene"
3:9312	3-Chlorohexadiene-1,3	3:8150	$\beta$ -Chloro-isopropyl acetate
3:0945	Chlorohexamethylethane	3:7747	$\beta$ -Chloro-isopropyl alcohol
3:7955	1-Chlorohexane	3:9610	$\alpha$ -Chloro-isopropylbenzene
3:7715	2-Chlorohexane	3:8705	4-Chloro-isopropylbenzene
3:7670	3-Chlorohexane	3:8605	4-Chloro-isopropylbenzene - bis-( $\beta$ -Chloro-isopropyl) ether
3:9395	6-Chlorohexanol-1	3:8775	2-Chloro-4-isopropyl-1-methyl- benzene
3:7735	3-Chlorohexatetraene-1,3,4,5	3:8770	3-Chloro-4-isopropyl-1-methyl- benzene
3:7630	1-Chlorohexene-1	3:9290	$\alpha$ -Chloroisopropyl-methyl- carbinol
3:7530	2-Chlorohexene-1	3:1293	4-Chloro-2-isopropyl-5-methyl- phenol
3:9334	3-Chlorohexene-1	3:0480	4-Chloro-5-isopropyl-2-methyl- phenol
3:7655	4-Chlorohexene-1	3:3220	2,4,6- <i>tris</i> -( $\alpha$ -Chloro-isopropyl)- trioxane-1,3,5
3:7665	5-Chlorohexene-1	3:0050	$\alpha$ -Chloro-isovaleric acid
3:7620	1-Chlorohexene-2	3:8144	$\alpha$ -Chloro-isovaleryl chloride
3:7675	4-Chlorohexene-2	3:9088	$\gamma$ -Chloro- $\beta$ -keto- <i>n</i> -butyryl chloride
3:0336	<i>cis</i> -1-Chlorohexene-3	3:0172	$\omega$ -Chlorolauryl alcohol
3:7535	3-Chlorohexene-3	3:3432	Chloromaleic acid
3:9395	$\omega$ -Chloro- <i>n</i> -hexyl alcohol	3:0280	Chloromaleic anhydride
3:9320	1-Chlorohexyne-1	3:6158	Chloromaleyl (di)chloride
3:3130	2-Chlorohydroquinone	3:8725	<i>eso</i> -Chloromesitylene
3:1010	3-Chloro-2-hydroxybenzaldehyde	3:7005	Chloromethane
3:0960	4-Chloro-2-hydroxybenzaldehyde	3:8210	3-Chloro-3-methoxyethylpentane
3:2800	5-Chloro-2-hydroxybenzaldehyde	3:5356	Chloromethyl acetate
3:4095	2-Chloro-3-hydroxybenzaldehyde	3:9660	$\omega$ -Chloro- <i>o</i> -methylacetophenone
3:3780	4-Chloro-3-hydroxybenzaldehyde	3:1130	$\omega$ -Chloro- <i>p</i> -methylacetophenone
3:3350	6-Chloro-3-hydroxybenzaldehyde	3:8340	$\gamma$ -Chloro- $\beta$ -methylallyl alcohol
3:4280	2-Chloro-4-hydroxybenzaldehyde	3:4435	3-Chloro-2-methylbenzoic acid
3:4065	3-Chloro-4-hydroxybenzaldehyde	3:4700	4-Chloro-2-methylbenzoic acid
3:3350	2-Chloro-5-hydroxybenzaldehyde	3:4670	5-Chloro-2-methylbenzoic acid
3:4745	3-Chloro-2-hydroxybenzoic acid	3:3275	6-Chloro-2-methylbenzoic acid
3:4908	4-Chloro-2-hydroxybenzoic acid	3:4915	4-Chloro-3-methylbenzoic acid
3:4705	5-Chloro-2-hydroxybenzoic acid	3:4715	5-Chloro-3-methylbenzoic acid
3:4610	6-Chloro-2-hydroxybenzoic acid	3:4615	6-Chloro-3-methylbenzoic acid
3:4395	2-Chloro-3-hydroxybenzoic acid	3:4355	2-Chloro-4-methylbenzoic acid
3:4933	4-Chloro-3-hydroxybenzoic acid	3:4900	3-Chloro-4-methylbenzoic acid
3:4720	6-Chloro-3-hydroxybenzoic acid	3:9570	$\alpha$ -(Chloromethyl)benzyl alcohol
3:4430	2-Chloro-4-hydroxybenzoic acid	3:7390	1-Chloro-3-methylbutadiene-1,2
3:4675	3-Chloro-4-hydroxybenzoic acid	3:9200	1-Chloro-2-methylbutadiene-1,3
3:1757	3-Chloro-2-hydroxybiphenyl	3:7290	3-Chloro-2-methylbutadiene-1,3
3:8980	5-Chloro-2-hydroxybiphenyl	3:7355	4-Chloro-2-methylbutadiene-1,3
3:1900	3-Chloro-4-hydroxybiphenyl	3:7355	1-Chloro-3-methylbutadiene-1,3
3:4262	4'-Chloro-4-hydroxybiphenyl	3:7290	2-Chloro-3-methylbutadiene-1,3
3:9185	$\beta$ -Chloro- $\beta'$ -hydroxydiethyl ether	3:7390	4-Chloro-2-methylbutadiene-2,3
3:6517	$\beta$ -Chloro- $\beta'$ -hydroxy-isopropyl acetate	3:7345	1-Chloro-2-methylbutane
3:6648	$\beta$ -Chloro- $\gamma$ -hydroxy- <i>n</i> -propyl acetate	3:7220	2-Chloro-2-methylbutane
3:6775	$\gamma$ -Chloro- $\beta$ -hydroxy- <i>n</i> -propyl acetate	3:7275	3-Chloro-2-methylbutane
3:7905	$\beta$ -Chloroisobutyl alcohol	3:7365	4-Chloro-2-methylbutane
3:7120	$\alpha$ -Chloroisobutylene	3:7365	1-Chloro-3-methylbutane
3:7145	$\gamma$ -Chloroisobutylene	3:8175	1-Chloro-2-methylbutanol-2
3:7235	$\alpha$ -Chloro-isobutylaldehyde	3:8030	3-Chloro-2-methylbutanol-2
3:0112	$\beta$ -Chloro-isobutylaldehyde	3:8335	4-Chloro-2-methylbutanol-2
3:0235	$\alpha$ -Chloro-isobutyric acid	3:9290	2-Chloro-2-methylbutanol-3
3:0132	$\beta$ -Chloro-isobutyric acid	3:9269	1-Chloro-2-methylbutanol-3
3:5385	$\alpha$ -Chloro-isobutyryl chloride	3:7597	2-Chloro-2-methylbutanol-3
3:9101	$\beta$ -Chloro-isobutyryl chloride		
3:1615	$\alpha$ -Chloroisocrotonic acid		
3:1300	$\beta$ -Chloroisocrotonic acid		
3:0372	$\alpha^2$ -Chloroisodurene		

- 3:9740 8-Chloro-2,6-dimethyloctane  
 3:9714 4-Chloro-3,7-dimethyloctene-2  
 3:9714 5-Chloro-2,6-dimethyloctene-6  
 3:9440 4-Chloro-2,2-dimethylpentane  
 3:9442 2-Chloro-2,3-dimethylpentane  
 3:7970 3-Chloro-2,3-dimethylpentane  
 3:8153 5-Chloro-2,3-dimethylpentane  
 3:7750 2-Chloro-2,4-dimethylpentane  
 3:8153 1-Chloro-3,4-dimethylpentane  
 3:7725 4-Chloro-2,4-dimethylpentene-1  
 3:7605 3-Chloro-2,4-dimethylpentene-2  
 3:0418 4-Chloro-2,4-dimethylpentene-2  
 3:9418 2-Chloro-2,4-dimethylpentene-3  
 3:9218 4-Chloro-2,3-dimethylphenol  
 3:2115 5-Chloro-2,3-dimethylphenol  
 3:2460 5-Chloro-2,4-dimethylphenol  
 3:8784 6-Chloro-2,4-dimethylphenol  
 3:1822 4-Chloro-2,5-dimethylphenol  
 3:2180 4-Chloro-2,6-dimethylphenol  
 3:0158 2-Chloro-3,4-dimethylphenol  
 3:2705 5-Chloro-3,4-dimethylphenol  
 3:1754 6-Chloro-3,4-dimethylphenol  
 3:0844 2-Chloro-3,5-dimethylphenol  
 3:3505 4-Chloro-3,5-dimethylphenol  
 3:7200 1-Chloro-2,2-dimethylpropane  
 3:0440  $\beta$ -Chloro- $\alpha,\alpha$ -dimethylpropionic acid  
 3:9266  $\beta$ -Chloro- $\alpha,\alpha$ -dimethylpropionyl chloride  
 3:3585  $\alpha$ -Chloro-diphenylacetic acid  
 3:0885  $\alpha$ -Chloro-diphenylacetyl chloride  
 3:0060  $\alpha$ -Chlorodiphenylmethane  
 3:0870 Chloro-diphenyl-methyl-methane  
 3:8810 1-Chlorododecane  
 3:0172 12-Chlorododecanol-1  
 3:0172  $\omega$ -Chloro-*n*-dodecyl alcohol  
 3:9702  $\omega$ -Chlorodurene  
 3:5358 3-Chloro-1,2-epoxypropane  
 3:7015 Chloroethane  
 3:5552  $\beta$ -Chloroethanol  
 3:5552 2-Chloroethanol-1  
 3:7010 Chloroethene  
 3:6210  $\alpha,\alpha$ -bis-( $\beta$ -Chloroethoxy)ethane  
 3:6655  $\alpha,\beta$ -bis-( $\beta$ -Chloroethoxy)ethane  
 3:9185 2-( $\beta$ -Chloroethoxy)ethanol-1  
 3:6655  $\beta$ -( $\beta$ -Chloroethoxy)ethyl  $\beta$ -chloroethyl ether  
 3:7625  $\alpha$ -Chloroethyl acetate  
 3:5735  $\beta$ -Chloroethyl acetate  
 3:5552  $\beta$ -Chloroethyl alcohol  
 3:9480  $\alpha$ -Chloroethyl *n*-amyl ether  
 3:8667  $\alpha$ -Chloroethylbenzene  
 3:8712  $\beta$ -Chloroethylbenzene  
 3:8712  $\omega$ -Chloroethylbenzene  
 3:8550 *o*-Chloroethylbenzene  
 3:8570 *p*-Chloroethylbenzene  
 3:8860  $\beta$ -Chloroethyl benzoate  
 3:7720 1-Chloro-2-ethylbutane  
 3:9396  $\alpha$ -Chloroethyl *n*-butyl ether  
 3:6230  $\beta$ -Chloroethyl chloroacetate  
 3:5780  $\beta$ -Chloroethyl chlorocarbonate  
 3:9150  $\alpha$ -Chloroethyl  $\beta$ -chloroethyl ether  
 3:5780  $\beta$ -Chloroethyl chloroformate  
 3:5900  $\alpha$ -Chloroethyl chloromethyl ketone  
 3:8030  $\alpha$ -Chloroethyl-dimethyl-carbinol  
 3:8335  $\beta$ -Chloroethyl-dimethyl-carbinol  
 3:7595 bis-( $\alpha$ -Chloroethyl) ether  
 3:6025 bis-( $\beta$ -Chloroethyl) ether  
 3:8500  $\beta$ -Chloroethyl-ethyl-carbinol  
 3:7305  $\alpha$ -Chloroethyl ethyl ether  
 3:7463  $\beta$ -Chloroethyl ethyl ether  
 3:7935  $\alpha$ -Chloroethyl ethyl ketone  
 3:9288  $\beta$ -Chloroethyl ethyl ketone  
 3:9646 3-Chloro-3-ethylheptane  
 3:9648 4-Chloro-4-ethylheptane  
 3:8370 1-Chloro-2-ethylhexane  
 3:9552 1-Chloro-3-ethylhexane  
 3:8223 3-Chloro-3-ethylhexane  
 3:8510 1-Chloro-4-ethylhexene-3  
 3:9185  $\alpha$ -Chloroethyl  $\beta$ -hydroxyethyl ether  
 3:5330 Chloroethylidene (di)chloride  
 3:7150  $\alpha$ -Chloroethyl methyl ether  
 3:7265  $\beta$ -Chloroethyl methyl ether  
 3:7593  $\alpha$ -Chloroethyl methyl ketone  
 3:7640  $\beta$ -Chloroethyl methyl ketone  
 3:8210 3-Chloro-3-ethyl-2-methyl-pentane  
 3:8115 2-Chloro-3-ethyl-3-methyl-pentene-1  
 3:9734 3-Chloro-3-ethyloctane  
 3:9736 4-Chloro-4-ethyloctane  
 3:9406 1-Chloro-3-ethylpentadiene-1,2  
 3:9438 2-Chloro-3-ethylpentane  
 3:8055 3-Chloro-3-ethylpentane  
 3:9410 1-Chloro-3-ethylpentene-1  
 3:9770  $\beta$ -Chloroethyl  $\beta'$ -phenoxyethyl ether  
 3:0165  $\beta$ -Chloroethyl phenyl ether  
 3:9664  $\alpha$ -Chloroethyl phenyl ketone  
 3:1115  $\beta$ -Chloroethyl phenyl ketone  
 3:7525  $\alpha$ -Chloroethyl *n*-propyl ether  
 3:6510  $\beta$ -Chloroethyl trichloroacetate  
 3:7464  $\beta$ -Chloroethyl vinyl ether  
 3:7000 Chloroethyne  
 3:9494 Chloroethynylbenzene  
 3:5050 Chloroform  
 3:4853 Chlorofumaric acid  
 3:6105 Chlorofumaryl (di)chloride  
 3:9803 1-Chlorohendecane  
 3:0100 1-Chloroheptadecane  
 3:8085 1-Chloroheptadiene-1,6  
 3:8250 1-Chloroheptane  
 3:9432 2-Chloroheptane  
 3:8080 3-Chloroheptane  
 3:8095 4-Chloroheptane  
 3:0013 7-Chloroheptanol-1  
 3:8219 1-Chloroheptene-1  
 3:7988 2-Chloroheptene-1  
 3:9412 3-Chloroheptene-1  
 3:8050 4-Chloroheptene-2  
 3:8023 4-Chloroheptene-3  
 3:0013  $\omega$ -Chloro-*n*-heptyl alcohol  
 3:8032 1-Chloroheptyne-1

3:9606	$\beta$ -Chloro- $\beta$ -methylstyrene	3:9514	1-Chloro-octyne-2
3:8152	2-(Chloromethyl)tetrahydrofuran	3:0525	$\omega$ -Chloropalmityl alcohol
3:9660	Chloromethyl <i>o</i> -tolyl ketone	3:9890	1-Chloropentadecane
3:1130	Chloromethyl <i>p</i> -tolyl ketone	3:7369	3-Chloropentadiene-1,3
3:2300	2,4,6-tris-(Chloromethyl)tri-oxane-1,3,5	3:7460	1-Chloropentane
3:8110	Chloromethyl-vinyl-carbinol	3:7325	2-Chloropentane
3:3934	Chloromethyl <i>p</i> -xenyl ketone	3:7330	3-Chloropentane
3:0375	$\omega$ -Chloromyristyl alcohol	3:9295	5-Chloropentanol-1
3:6878	1-Chloronaphthalene	3:8225	1-Chloropentanol-2
3:1285	2-Chloronaphthalene	3:8500	1-Chloropentanol-3
3:4330	2-Chloronaphthoic acid-1	3:8217	1-Chloropentane-2
3:4936	4-Chloronaphthoic acid-1	3:7893	3-Chloropentanone-2
3:4944	5-Chloronaphthoic acid-1	3:8243	4-Chloropentanone-2
3:4845	6-Chloronaphthoic acid-1	3:9267	5-Chloropentanone-2
3:4942	7-Chloronaphthoic acid-1	3:9268	1-Chloropentanone-3
3:4680	8-Chloronaphthoic acid-1	3:7935	2-Chloropentanone-3
3:4885	1-Chloronaphthoic acid-2	3:7420	1-Chloropentene-1
3:4928	3-Chloronaphthoic acid-2	3:7280	2-Chloropentene-1
3:4952	5-Chloronaphthoic acid-2	3:7260	3-Chloropentene-1
3:4948	8-Chloronaphthoic acid-2	3:7350	4-Chloropentene-1
3:1490	2-Chloronaphthol-1	3:7410	5-Chloropentene-1
3:1470	3-Chloronaphthol-1	3:7470	1-Chloropentene-2
3:3720	4-Chloronaphthol-1	3:7285	2-Chloropentene-2
3:3960	5-Chloronaphthol-1	3:7240	3-Chloropentene-2
3:2615	6-Chloronaphthol-1	3:7400	4-Chloropentene-2
3:3810	7-Chloronaphthol-1	3:7455	5-Chloropentene-2
3:1610	8-Chloronaphthol-1	3:7455	1-Chloropentene-3
3:1700	1-Chloronaphthol-2	3:7400	2-Chloropentene-3
3:2545	3-Chloronaphthol-2	3:2990	<i>p</i> -Chlorophenacyl chloride
3:3045	4-Chloronaphthol-2	3:8735	<i>o</i> -Chlorophenetole
3:3945	5-Chloronaphthol-2	3:6323	<i>m</i> -Chlorophenetole
3:3500	6-Chloronaphthol-2	3:0090	<i>p</i> -Chlorophenetole
3:3925	7-Chloronaphthol-2	3:0165	$\omega$ -Chlorophenetole
3:2965	8-Chloronaphthol-2	3:5980	<i>o</i> -Chlorophenol
3:4704	3-Chloro- $\beta$ -naphthoquinone	3:0255	<i>m</i> -Chlorophenol
3:4704	3-Chloronaphthoquinone-1,2	3:0475	<i>p</i> -Chlorophenol
3:4090	4-Chloronaphthoquinone-1,2	3:4260	<i>o</i> -Chlorophenoxyacetic acid
3:3580	2-Chloronaphthoquinone-1,4	3:3325	<i>m</i> -Chlorophenoxyacetic acid
3:4492	5-Chloronaphthoquinone-1,4	3:4375	<i>p</i> -Chlorophenoxyacetic acid
3:3145	6-Chloronaphthoquinone-1,4	3:2640	2-Chlorophenylacetic acid
3:8719	1-Chlorononane	3:1910	3-Chlorophenylacetic acid
3:8635	2-Chlorononane	3:3135	4-Chlorophenylacetic acid
3:9638	3-Chlorononane	3:1618	$\alpha$ -Chloro- $\alpha$ -phenyl-acetophenone
3:9640	5-Chlorononane	3:3934	$\omega$ -Chloro- <i>p</i> -phenylacetophenone
3:0170	9-Chlorononanol-1	3:9497	<i>o</i> -Chlorophenylacetylene
3:0170	$\omega$ -Chloro- <i>n</i> -nonyl alcohol	3:9500	<i>m</i> -Chlorophenylacetylene
3:9618	1-Chlorooctyne-1	3:0590	<i>p</i> -Chlorophenylacetylene
3:0095	1-Chloro-octadecane	3:9494	$\alpha$ -Chloro- $\beta$ -phenylacetylene
3:0985	18-Chloro-octadecanol-1	3:9494	$\omega$ -Chlorophenylacetylene
3:0985	$\omega$ -Chloro- <i>n</i> -octadecyl alcohol	3:9859-A	<i>o</i> -Chlorophenyl <i>m</i> -chlorophenyl ketone
3:9506	3-Chloro-octadiene-1,3	3:1565	<i>o</i> -Chlorophenyl <i>p</i> -chlorophenyl ketone
3:8585	1-Chloro-octane	3:3415	<i>m</i> -Chlorophenyl <i>p</i> -chlorophenyl ketone
3:8378	2-Chloro-octane	3:8735	<i>o</i> -Chlorophenyl ethyl ether
3:9538	4-Chloro-octane	3:6323	<i>m</i> -Chlorophenyl ethyl ether
3:9590	8-Chloro-octanol-1	3:0090	<i>p</i> -Chlorophenyl ethyl ether
3:8346	2-Chloro-octene-1	3:0340	<i>p</i> -Chlorophenyl ethyl ketone
3:9518	3-Chloro-octene-1	3:6255	<i>o</i> -Chlorophenyl methyl ether
3:8345	2-Chloro-octene-2	3:6195	<i>m</i> -Chlorophenyl methyl ether
3:8185	4-Chloro-octene-2	3:6300	<i>p</i> -Chlorophenyl methyl ether
3:8230	4-Chloro-octene-4		
3:9590	$\omega$ -Chloro- <i>n</i> -octyl alcohol		
3:9510	1-Chloro-octyne-1		

- 3:9214 2-(Chloromethyl)butene-1  
 3:7303 1-Chloro-2-methylbutene-1  
 3:7300 3-Chloro-2-methylbutene-1  
 3:7215 1-Chloro-3-methylbutene-1  
 3:7485 1-Chloro-2-methylbutene-2  
 3:7335 3-Chloro-2-methylbutene-2  
 3:7465 4-Chloro-2-methylbutene-2  
 3:7215 4-Chloro-2-methylbutene-3  
 3:7155 3-Chloro-3-methylbutyne-1  
 3:7155 2-Chloro-2-methylbutyne-3  
 3:8718  $\alpha$ -Chloro- $\alpha$ -methyl-*n*-butyric acid  
 3:0050  $\alpha$ -Chloro- $\beta$ -methyl-*n*-butyric acid  
 3:5670  $\alpha$ -Chloro- $\alpha$ -methyl-*n*-butyryl chloride  
 3:8144  $\alpha$ -Chloro- $\beta$ -methyl-*n*-butyryl chloride  
 3:5275 Chloromethyl chlorocarbonate  
 3:5275 Chloromethyl chloroformate  
 3:2990 Chloromethyl *p*-chlorophenyl ketone  
 3:9201 2-(Chloromethyl)-1,3-dichlorobutene-1  
 3:7657 3-Chloro-2-methyl-1,2-epoxypropane  
 3:5245 *bis*-(Chloromethyl) ether  
 3:5358 (Chloromethyl)ethylene oxide  
 3:7195 Chloromethyl ethyl ether  
 3:8012 Chloromethyl ethyl ketone  
 3:8175 Chloromethyl-ethyl-methyl-carbinol  
 3:8370 3-(Chloromethyl)heptane  
 3:8100 2-Chloro-2-methylheptane  
 3:0540 6-Chloro-2-methylheptane  
 3:9544 3-Chloro-3-methylheptane  
 3:9548 3-Chloro-4-methylheptane  
 3:9550 4-Chloro-4-methylheptane  
 3:8205 4-Chloro-6-methylheptene-1  
 3:9520 6-Chloro-2-methylheptene-2  
 3:9524 4-Chloro-3-methylheptene-2  
 3:9525 4-Chloro-6-methylheptene-2  
 3:9526 5-Chloro-4-methylheptene-3  
 3:9525 4-Chloro-2-methylheptene-5  
 3:8205 4-Chloro-2-methylheptene-6  
 3:9516 3-Chloro-3-methylheptyne-4  
 3:7945 2-Chloro-2-methylhexane  
 3:7985 5-Chloro-2-methylhexane  
 3:8155 1-Chloro-3-methylhexane  
 3:9434 2-Chloro-3-methylhexane  
 3:7950 3-Chloro-3-methylhexane  
 3:9436 4-Chloro-3-methylhexane  
 3:7730 4-Chloro-5-methylhexene-1  
 3:9414 4-Chloro-3-methylhexene-2  
 3:7890 4-Chloro-5-methylhexene-2  
 3:7890 3-Chloro-2-methylhexene-4  
 3:7730 3-Chloro-2-methylhexene-5  
 3:9402 5-Chloro-5-methylhexen-1-yne-3  
 3:9402 2-Chloro-2-methylhexen-5-yne-3  
 3:8795 1-Chloromethyl-4-isopropylbenzene  
 3:0563 *bis*-(Chloromethyl) ketone  
 3:7747 Chloromethyl-methyl-carbinol  
 3:9614 2-Chloro-6-methyl-5-methyleneheptene-2  
 3:7085 Chloromethyl methyl ether  
 3:9560 4-(Chloromethyl)-3-methylhexane  
 3:0250 1-(Chloromethyl)naphthalene  
 3:0747 2-(Chloromethyl)naphthalene  
 3:9730 4-Chloro-4-methylnonane  
 3:9732 5-Chloro-5-methylnonane  
 3:9710 3-Chloro-3-methylnonyne-4  
 3:9642 3-Chloro-3-methyloctane  
 3:9644 4-Chloro-4-methyloctane  
 3:9628 4-Chloro-7-methyloctene-2  
 3:9624 5-Chloro-4-methyloctene-3  
 3:9628 5-Chloro-2-methyloctene-6  
 3:9622 2-Chloro-2-methyloctyne-3  
 3:9314 1-Chloro-3-methylpentadiene-1,2  
 3:9316 1-Chloro-3-methylpentadiene-1,3  
 3:9318 2-Chloro-3-methylpentadiene-1,3  
 3:7720 3-(Chloromethyl)pentane  
 3:7563 1-Chloro-2-methylpentane  
 3:7490 2-Chloro-2-methylpentane  
 3:7565 3-Chloro-2-methylpentane  
 3:7495 4-Chloro-2-methylpentane  
 3:7695 5-Chloro-2-methylpentane  
 3:9348 1-Chloro-3-methylpentane  
 3:9350 2-Chloro-3-methylpentane  
 3:7585 3-Chloro-3-methylpentane  
 3:7660 3-Chloro-2-methylpentene-1  
 3:7500 4-Chloro-4-methylpentene-1  
 3:7915 5-Chloro-2-methylpentene-2  
 3:9338  
 3:7500  
 3:9322  
 3:9324  
 3:2280  
 3:0780  
 3:1815  
 3:8615  
 3:1055  
 3:1535  
 3:0700  
 3:6215  
 3:1025  
 3:0700  
 3:9570  
 3:9448  
 3:1212  
 3:7235  
 3:9112  
 3:7135  
 3:7045  
 3:9190  
 3:7905  
 3:9180  
 3:7752  
 3:7120  
 3:7145  
 3:8340  
 3:8225  
 3:8217  
 3:8742  
 3:9604  
 Chloromethyl-*n*-propyl-carbinol  
 Chloromethyl-*n*-propyl ketone  
 $\beta$ -Chloro- $\alpha$ -methylstyrene  
 $\alpha$ -Chloro- $\beta$ -methylstyrene

3:4020	3-Chloro-2,2,3-trimethylbutane		
3:7752	Chloro-trimethylcarbinol	3:3320	"DDD"
3:9039	$\beta$ -Chlorotrimethylene glycol	3:1890	" <i>o,p'</i> -DDD"
3:6648	$\beta$ -Chlorotrimethylene glycol acetate	3:3320	" <i>p,p'</i> -DDD"
3:9744	4-Chloro-2,4,6-trimethylheptane	3:3298	"DDT"
3:9654	3-Chloro-2,2,3-trimethylhexane	3:9965	" <i>o,o'</i> -DDT"
3:8113	4-Chloro-2,2,4-trimethylpentane	3:1820	" <i>o,p'</i> -DDT"
3:3560	1-Chloro-1,2,2-triphenylethylene	3:9867	" <i>m,p'</i> -DDT"
3:3560	"Chlorotriphenylethylene"	3:3298	" <i>p,p'</i> -DDT"
3:3410	$\alpha$ -Chlorotriphenylmethane	3:1076	Decachlorodiethyl ether
3:8803	1-Chloroundecane	3:9720	Decamethylene (di)chloride
3:8783	$\alpha$ -Chloro- <i>n</i> -valeric acid	3:5800	<i>n</i> -Decanoyl chloride
3:0270	$\beta$ -Chloro- <i>n</i> -valeric acid	3:8785	<i>n</i> -Decyl chloride
3:9270	$\gamma$ -Chloro- <i>n</i> -valeric acid	3:1618	Desyl chloride
3:0075	$\delta$ -Chloro- <i>n</i> -valeric acid	3:8085	Diallylcarbinyl chloride
3:5860	$\alpha$ -Chloro- <i>n</i> -valeryl chloride	3:9640	Di- <i>n</i> -butylcarbinyl chloride
3:9260	$\beta$ -Chloro- <i>n</i> -valeryl chloride	3:9732	Di- <i>n</i> -butyl-methyl-carbinyl chloride
3:9264	$\delta$ -Chloro- <i>n</i> -valeryl chloride	3:6110	"Dichloroacetal"
3:7070	1-Chloro-2-vinylacetylene	3:5180	Dichloroacetaldehyde
3:8715	$\alpha$ -Chlorovinylbenzene	3:6110	Dichloroacetaldehyde diethyl-acetal
3:8717	$\beta$ -Chlorovinylbenzene	3:5310	Dichloroacetaldehyde ethyl-alcoholate
3:0300	2-Chloro-xenene	3:5310	Dichloroacetaldehyde ethyl-hemiacetal
3:8910	3-Chloro-xenene	3:1085	Dichloroacetaldehyde hydrate
3:1912	4-Chloro-xenene	3:6208	Dichloroacetic acid
3:8710	$\omega$ -Chloro- <i>o</i> -xylene	3:6430	Dichloroacetic acid anhydride
3:8645	<i>vic.</i> -Chloro- <i>o</i> -xylene	3:5430	$\alpha,\alpha$ -Dichloroacetone
3:8675	<i>unsym.</i> -Chloro- <i>o</i> -xylene	3:0563	$\alpha,\alpha'$ -Dichloroacetone
3:8700	$\omega$ -Chloro- <i>m</i> -xylene	3:0563	<i>sym.</i> -Dichloroacetone
3:8590	<i>vic.</i> -Chloro- <i>m</i> -xylene	3:5430	<i>unsym.</i> -Dichloroacetone
3:8665	<i>unsym.</i> -Chloro- <i>m</i> -xylene	3:6835	$\omega,\omega$ -Dichloroacetophenone
3:8610	<i>sym.</i> -Chloro- <i>m</i> -xylene	3:5290	Dichloroacetyl chloride
3:8660	$\omega$ -Chloro- <i>p</i> -xylene	3:5010	Dichloroacetylene
3:8600	<i>iso</i> -Chloro- <i>p</i> -xylene	3:2265	$\alpha,\beta$ -Dichloroacrylic acid
3:2115	5-Chloro- <i>o</i> -3-xyleneol	3:1875	$\beta,\beta$ -Dichloroacrylic acid
3:2218	6-Chloro- <i>o</i> -3-xyleneol	3:4916	9,10-Dichloroanthracene
3:1764	5-Chloro- <i>o</i> -4-xyleneol	3:4916	<i>meso</i> -Dichloroanthracene
3:2705	6-Chloro- <i>o</i> -4-xyleneol	3:9399	2,4-Dichlorobenzal (di)chloride
3:0158	3-Chloro- <i>o</i> -4-xyleneol	3:0490	2,5-Dichlorobenzal (di)chloride
3:2180	5-Chloro- <i>m</i> -2-xyleneol	3:9398	2,6-Dichlorobenzal (di)chloride
3:8784	5-Chloro- <i>m</i> -4-xyleneol	3:0876	3,4-Dichlorobenzal (di)chloride
3:2460	6-Chloro- <i>m</i> -4-xyleneol	3:0370	3,5-Dichlorobenzal (di)chloride
3:3505	2-Chloro- <i>m</i> -5-xyleneol	3:1480	2,3-Dichlorobenzaldehyde
3:0844	6-Chloro- <i>m</i> -5-xyleneol	3:1890	2,4-Dichlorobenzaldehyde
3:1822	5-Chloro- <i>p</i> -2-xyleneol	3:1145	2,5-Dichlorobenzaldehyde
3:0330	Cinnamoyl chloride	3:1690	2,6-Dichlorobenzaldehyde
3:0010	Cinnamyl chloride	3:0550	3,4-Dichlorobenzaldehyde
3:9102	Crotonaldehyde dichloride	3:1475	3,5-Dichlorobenzaldehyde
3:5910	Crotonchloral	3:6055	<i>o</i> -Dichlorobenzene
3:1375	Crotonic acid dichloride	3:5960	<i>m</i> -Dichlorobenzene
3:7693	$\alpha$ -Crotonyl chloride	3:0990	<i>p</i> -Dichlorobenzene
3:7205	Crotonyl chloride	3:4965	4,6-Dichlorobenzenedicarboxylic acid-1,3
3:7685	Crotylidene (di)chloride	3:4985	2,5-Dichlorobenzenedicarboxylic acid-1,4
3:8795	Cuminyll chloride	3:4650	2,3-Dichlorobenzoic acid
3:8580	Cyclohexanecarboxylic acid chloride	3:4560	2,4-Dichlorobenzoic acid
3:9374	<i>cis</i> -Cyclohexene chlorohydrin	3:4340	2,5-Dichlorobenzoic acid
3:0175	<i>trans</i> -Cyclohexene chlorohydrin	3:4200	2,6-Dichlorobenzoic acid
3:8040	Cyclohexyl chloride	3:4925	3,4-Dichlorobenzoic acid
3:5770	Cyclohexyl chlorocarbonate		
3:5770	Cyclohexyl chloroformate		
3:7545	Cyclopentyl chloride		

- 3:6615 *o*-Chlorophenyl methyl ketone  
 3:6815 *m*-Chlorophenyl methyl ketone  
 3:6735 *p*-Chlorophenyl methyl ketone  
 3:1757 " *o*-Chloro-*o*'-phenylphenol "  
 3:8950 4-Chloro-2-phenylphenol  
 3:1757 6-Chloro-2-phenylphenol  
 3:1900 2-Chloro-4-phenylphenol  
 3:0715 *o*-Chlorophenyl phenyl ketone  
 3:2160 *m*-Chlorophenyl phenyl ketone  
 3:1914 *p*-Chlorophenyl phenyl ketone  
 3:9880 3-Chloro-3-phenylphthalide  
 3:9610 2-Chloro-2-phenylpropane  
 3:9604 1-Chloro-1-phenylpropene-1  
 3:9606 2-Chloro-1-phenylpropene-1  
 3:0010 3-Chloro-1-phenylpropene-1  
 3:8742 1-Chloro-2-phenylpropene-1  
 3:8737 1-Chloro-3-phenylpropene-1  
 3:9608 2-Chloro-3-phenylpropene-1  
 3:3956 *o*-Chlorophenylpropionic acid  
 3:4102 *m*-Chlorophenylpropionic acid  
 3:4265 *p*-Chlorophenylpropionic acid  
 3:4820 3-Chlorophthalic acid  
 3:4390 4-Chlorophthalic acid  
 3:3900 3-Chlorophthalic anhydride  
 3:2725 4-Chlorophthalic anhydride  
 3:0440 Chloropivalic acid  
 3:9266 Chloropivalyl chloride  
 3:7080 Chloroprene  
 3:5576 3-Chloropropanal-1  
 3:7040 1-Chloropropane  
 3:7025 2-Chloropropane  
 3:9039 3-Chloropropanediol-1,2  
 3:9039 2-Chloropropanediol-1,3  
 3:6840 3-Chloropropanediol-1,2 diacetate  
 3:6125 2-Chloropropanoic acid  
 3:0460 3-Chloropropanoic acid  
 3:7917 2-Chloropropanol-1  
 3:8285 3-Chloropropanol-1  
 3:7747 1-Chloropropanol-2  
 3:5425 1-Chloropropanone-2  
 3:9031 2-Chloropropen-2-*o*-1-1  
 3:7030 1-Chloropropene-1  
 3:7020 2-Chloropropene-1  
 3:7035 3-Chloropropene-1  
 3:5635 2-Chloropropen-2-*o*-1-1  
 3:5820 3-Chloropropen-2-*o*-1-1  
 3:5635 2-Chloropropen-1-*o*-1-3  
 3:1685 Chloropropionic acid  
 3:5160  $\alpha$ -Chloropropionaldehyde  
 3:5576  $\beta$ -Chloropropionaldehyde  
 3:9190  $\beta$ -Chloropropionaldehyde diethyl acetal  
 3:6125  $\alpha$ -Chloropropionic acid  
 3:0460  $\beta$ -Chloropropionic acid  
 3:5320  $\alpha$ -Chloropropionyl chloride  
 3:5690  $\beta$ -Chloropropionyl chloride  
 3:9664  $\alpha$ -Chloropropiophenone  
 3:1115  $\beta$ -Chloropropiophenone  
 3:0340 4-Chloropropiophenone  
 3:8180  $\beta$ -Chloro-*n*-propyl acetate  
 3:8310  $\gamma$ -Chloro-*m*-propyl acetate  
 3:7917  $\beta$ -Chloro-*n*-propyl alcohol  
 3:8285  $\gamma$ -Chloro-*n*-propyl alcohol  
 3:8777  $\gamma$ -Chloro-*n*-propylbenzene  
 3:6010  $\gamma$ -Chloro-*n*-propyl chlorocarbonate  
 3:6010  $\gamma$ -Chloro-*n*-propyl chloroformate  
 3:9038  $\gamma$ -Chloropropylene glycol  
 3:6775  $\gamma$ -Chloropropylene glycol  $\alpha$ -acetate  
 3:6517  $\gamma$ -Chloropropylene glycol  $\beta$ -acetate  
 3:6340  $\gamma$ -Chloropropylene glycol diacetate  
 3:5358  $\gamma$ -Chloropropylene oxide  
 3:8610 *bis*-( $\beta$ -Chloro-*n*-propyl) ether  
 3:8745 *bu*-( $\gamma$ -Chloro-*n*-propyl) ether  
 3:9742 4-Chloro-4-*n*-propylheptane  
 3:5630  $\alpha$ -Chloropropylidene (di)-chloride  
 3:5660  $\beta$ -Chloropropylidene (di)-chloride  
 3:7893  $\alpha$ -Chloro-*n*-propyl methyl ketone  
 3:8243  $\beta$ -Chloro-*n*-propyl methyl ketone  
 3:9267  $\gamma$ -Chloro-*n*-propyl methyl ketone  
 3:8820  $\gamma$ -Chloro-*n*-propyl phenyl ether  
 3:2650 2,4,6-*tris*-( $\beta$ -Chloro-*n*-propyl)-trioxane-1,3,5  
 3:7100 3-Chloropropyn-1  
 3:0745 3-Chloropyrocatechol  
 3:2470 4-Chloropyrocatechol  
 3:1100 Chloroquinone  
 3:2690 2-Chlororesorcinol  
 3:3190 4-Chlororesorcinol  
 3:3530 5-Chlororesorcinol  
 3:1010 3-Chlorosalicylaldehyde  
 3:9960 4-Chlorosalicylaldehyde  
 4:2800 5-Chlorosalicylaldehyde  
 3:4745 3-Chlorosalicylic acid  
 3:4908 4-Chlorosalicylic acid  
 3:4705 5-Chlorosalicylic acid  
 3:4610 6-Chlorosalicylic acid  
 3:0955 *w*-Chlorostearyl alcohol  
 3:8215  $\alpha$ -Chlorostyrene  
 3:8717  $\beta$ -Chlorostyrene  
 3:8717 *w*-Chlorostyrene  
 3:4995 Chloroterephthalic acid  
 3:9874 1-Chlorotetradecane  
 3:0375 14-Chlorotetradecanol-1  
 3:0375 *w*-Chloro-*n*-tetradecyl alcohol  
 3:0945 1-Chloro-2,2,3,3-tetramethylbutane  
 3:1293 *p*-Chlorothymol  
 3:5335  $\alpha$ -Chlorotoluene  
 3:8535 *w*-Chlorotoluene  
 3:8245 *o*-Chlorotoluene  
 3:8275 *m*-Chlorotoluene  
 3:8287 *p*-Chlorotoluene  
 3:2640 *o*-Chloro- $\alpha$ -toluic acid  
 3:1910 *m*-Chloro- $\alpha$ -toluic acid  
 3:3135 *p*-Chloro- $\alpha$ -toluic acid  
 3:9859 1-Chlorotridecane  
 3:4555 5-Chlorotrimellitic acid  
 3:4975 Chlorotrimelic acid  
 3:8725 2-Chloro-1,3,5-trimethylbenzene

① 4,6-Dichloro-2-methylphenyl acetate: m.p. 28.5°, b.p. 254° (1). [From  $\bar{C}$  with excess  $Ac_2O$  + a drop of conc.  $H_2SO_4$  htd. 4 hrs. at 100° (1).]

② 4,6-Dichloro-2-methylphenyl benzoate: m.p. 114°, h.p. 240° (1). [From  $\bar{C}$  with benzoyl chlorido (1).]

3:1920 (1) Bures, *Chem. Listy* 21, 108-114, 148-162, 221-227, 261-265 (1927); *Cent.* 1927, II 1344; *C.A.* 22, 63 (1928). (2) Zincke, *Ann.* 417, 190, 206-207, 221-222 (1918). (3) Martini, *Gazz. chim. ital.* 29, II 60-61 (1899). (4) Claus, Schweitzer, *Ber.* 19, 927-929 (1886). (5) Chulkov, Parini, Barshev, *Org. Chem. Ind. (U.S.S.R.)* 3, 410-412 (1937); *Cent.* 1938, II 305; *C.A.* 31, 7047 (1937). (6) Huston, Neeley, *J. Am. Chem. Soc.* 57, 2177 (1935). (7) Claus, Riemann, *Ber.* 16, 1601-1602 (1883). (8) Tanaka, Morikawa, Sakamoto, *J. Chem. Soc. Japan* 51, 275-277 (1930), *C.A.* 26, 706 (1932). (9) Korczynski, *Cent.* 1909, II 806. (10) Anschütz, *Ann.* 454, 108 (1927).

(11) Weiler, Better (to I.G.), *Ger.* 557,450, Aug. 24, 1931; *Cent.* 1932, II 2371. (12) Weiler (to I.G.), *Ger.* 548,822, April 20, 1932; *Cent.* 1932, II 799.

3:1025 3-CHLORO-4-METHYLPHENOL  
(3-Chloro-*p*-cresol)


 $C_7H_7OCl$ 

Beil. VI-402

 VI<sub>1</sub>-

 VI<sub>2</sub>-

M.P. 55° (1) (2) B.P. 228° at 760 mm. (2)  
229° at 735 mm. (1)

Long colorless ndls., markedly sol. in aq. and volatile with steam (1). — Eas. sol. alc., ether, or  $C_6H_6$ .

[For prepn. (77% yield) from 3-chloro-4-methylaniline [Beil. XII-983] via diazo reaction see (1).]

$\bar{C}$  dislyd. in 20% NaOH and shaken with  $(CH_3)_2SO_4$  gives 95% yield of corresponding methyl ether, viz., 3-chloro-4-methylanisole, b.p. 212° (1). [Oxidn. of this ether with dil. aq.  $KMnO_4$  yields (1) 2-chloro-4-methoxybenzoic acid [Beil. X-175], ndls. from aq., m.p. 208° (1).]

3:1925 (1) Ullmann, Wagner, *Ann.* 355, 367-368 (1907). (2) Badische Anilin und Soda-fabrik, *Ger.* 156,333, Nov. 14, 1904; *Cent.* 1904, II 1672.

3:1040 o-XYLYLENE (DI)CHLORIDE  
( $\omega,\omega'$ -Dichloro-*o*-xylene)


 $C_8H_8Cl_2$ 

Beil. V-364

 V<sub>1</sub>-

 V<sub>2</sub>-(283)

M.P. 55° (1) (2) B.P. 239-241° (3)  
54.6-54.8° (3) 130-135° at 19 mm. (2)  
54-55° cor. (5)

Cryst. (from pet. eth.). — Sublimes. — Sol. alc., ether,  $CHCl_3$ , lgr. Powerful lachry-mator.

[For prepn. from *o*-xyleneglycol + boilg. conc.  $HCl$  see (3); from *o*-xylene (1:7430) +  $PCl_5$  at 190° see (3) (4); from *o*-xylene (1:7430) +  $Cl_2$  in sunlight see (1); for formn. of  $\bar{C}$  (13%) during chloromethylation of benzyl chloride (3:8535) see (5).]

$\bar{C}$  on oxidn. with  $KMnO_4$  yields phthalic ac. (1:0820).

3:1049 (1) Radziewanowski, Schramm, *Cent.* 1893, I 1919. (2) Quelet, *Bull. soc. chim.* (4) 53, 223 (1934). (3) Colson, *Ann. chim.* (6) 6, 108-109 (1885). (4) Colson, Gautier, *Ann. chim.* (6) 11, 22 (1887). (5) Kulka, *Can. J. Research* 23-B, 107 (1945).

- 3:4840 3,5-Dichlorobenzoic acid  
 3:0717 2,2'-Dichlorobenzophenone  
 3:9859-A 2,3'-Dichlorobenzophenone  
 3:0925 2,4-Dichlorobenzophenone  
 3:1565 2,4'-Dichlorobenzophenone  
 3:2340 2,5-Dichlorobenzophenone  
 3:2285 2,6-Dichlorobenzophenone  
 3:3860 3,3'-Dichlorobenzophenone  
 3:3070 3,4-Dichlorobenzophenone  
 3:3415 3,4'-Dichlorobenzophenone  
 3:1595 3,5-Dichlorobenzophenone  
 3:4270 4,4'-Dichlorobenzophenone  
 3:2855 *o*-Dichlorobenzoquinone  
 3:3750 *m*-Dichlorobenzoquinone  
 3:4470 *p*-Dichlorobenzoquinone  
 3:2855 2,3-Dichlorobenzoquinone-1,4  
 3:4470 2,5-Dichlorobenzoquinone-1,4  
 3:3750 2,6-Dichlorobenzoquinone-1,4  
 3:0410 2,6-Dichlorobenzyl chloride  
 3:6795 3,4-Dichlorobenzyl chloride  
 3:0350 3,5-Dichlorobenzyl chloride  
 3:9040 Dichlorobiacetylene  
 3:2570 *d,l*- $\alpha,\alpha'$ -Dichlorobiphenyl  
 3:4854 *meso*- $\alpha,\alpha'$ -Dichlorobiphenyl  
 3:1325 2,2'-Dichlorobiphenyl  
 3:9850 2,3-Dichlorobiphenyl  
 3:0670 2,4'-Dichlorobiphenyl  
 3:9854 2,5-Dichlorobiphenyl  
 3:0180 3,3'-Dichlorobiphenyl  
 3:0685 3,4-Dichlorobiphenyl  
 3:0360 3,5-Dichlorobiphenyl  
 3:4300 4,4'-Dichlorobiphenyl  
 3:9057 1,2-Dichlorobutadiene-1,3  
 3:6220 2,3-Dichlorobutadiene-1,3  
 3:0010 1,4-Dichlorobutadiene-1,3  
 3:9102 2,3-Dichlorobutanal-1  
 3:7550 1,1-Dichlorobutane  
 3:7680 1,2-Dichlorobutane  
 3:7925 1,3-Dichlorobutane  
 3:5835 1,4-Dichlorobutane  
 3:7415 2,2-Dichlorobutane  
 3:7615 *d,l*-2,3-Dichlorobutane  
 3:7580 *meso*-2,3-Dichlorobutane  
 3:9145 1,3-Dichlorobutan-2-ol  
 3:5900 1,3-Dichlorobutanone-2  
 3:7650 1,3-Dichlorobutene-1  
 3:9074 2,3-Dichlorobutene-1  
 3:5350 3,4-Dichlorobutene-1  
 3:7685 1,1-Dichlorobutene-2  
 3:5360 1,2-Dichlorobutene-2 (low-boilg. isomer)  
 3:5615 1,2-Dichlorobutene-2 (high-boilg. isomer)  
 3:5550 1,3-Dichlorobutene-2  
 3:5725 1,4-Dichlorobutene-2  
 3:5500 *cis*-2,3-Dichlorobutene-2  
 3:7395 *trans*-2,3-Dichlorobutene-2  
 3:5550 2,4-Dichlorobutene-2  
 3:5550 1,2-Dichlorobutene-3  
 3:5977 *sym.*-Dichloro-*tert*-butyl alcohol  
 3:5772 *unsym.*-Dichloro-*tert*-butyl alcohol  
 3:9102  $\alpha,\beta$ -Dichloro-*n*-butyraldehyde  
 3:1903  $\alpha,\beta$ -Dichloro-*n*-butyric acid (h.-m. isomer)  
 3:1375  $\alpha,\beta$ -Dichloro-*n*-butyric acid (l.-m. isomer)  
 3:2192 3,5-Dichlorocatechol  
 3:3525 4,5-Dichlorocatechol  
 3:9218 1,3-Dichloro-2-(chloromethyl)-butane  
 3:2675 1,3-Dichloro-2,2-*bis*-(chloromethyl)propane  
 3:9066 1,3-Dichloro-2-(chloromethyl)-propane-1  
 3:1890 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane  
 3:1925 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene  
 3:9863 1,1-Dichloro-2-(*m*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene  
 3:3320 1,1-Dichloro-2,2-*bis*-(*p*-chlorophenyl)ethane  
 3:2438 1,1-Dichloro-2,2-*bis*-(*p*-chlorophenyl)ethylene  
 3:2910 4,5-Dichloro-*o*-cresol  
 3:1020 4,6-Dichloro-*o*-cresol  
 3:1205 2,4-Dichloro-*m*-cresol  
 3:0150 2,6-Dichloro-*m*-cresol  
 3:1745 4,6-Dichloro-*m*-cresol  
 3:0100 2,6-Dichloro-*p*-cresol  
 3:9720 1,10-Dichlorodecane  
 3:7595  $\alpha,\alpha'$ -Dichlorodiethyl ether  
 3:5640  $\alpha,\beta$ -Dichlorodiethyl ether  
 3:9150  $\alpha,\beta'$ -Dichlorodiethyl ether  
 3:6025  $\beta,\beta'$ -Dichlorodiethyl ether  
 3:9724 3,4-Dichloro-3,4-diethylhexane  
 3:4970 2,5-Dichloro-3,6-dihydroxybenzoquinone-1,4  
 3:8605  $\beta,\beta'$ -Dichloro-diisopropyl ether  
 3:4325 3,3-Dichloro-2,2-dimethylbutane  
 3:8132 4,4-Dichloro-2,2-dimethylbutane  
 3:4570 2,3-Dichloro-2,3-dimethylbutane  
 3:8132 1,1-Dichloro-3,3-dimethylbutane  
 3:5245 *sym.*-Dichlorodimethyl ether  
 3:0155 2,6-Dichloro-2,6-dimethylheptane  
 3:1650 2,5-Dichloro-2,5-dimethylhexane  
 3:8315 3,4-Dichloro-3,4-dimethylhexane  
 3:9504 2,5-Dichloro-2,5-dimethylhexyne-3  
 3:0840 2,7-Dichloro-2,7-dimethyloctane  
 3:8516 4,5-Dichloro-2,2-dimethylpentane  
 3:9428 2,4-Dichloro-2,4-dimethylpentane  
 3:7610 3,3-Dichloro-2,4-dimethylpentane  
 3:9130 1,5-Dichloro-3,3-dimethylpentane  
 3:8516 1,2-Dichloro-4,4-dimethylpentane  
 3:9105 2,3-Dichlorodioxane-1,4  
 3:2442 5,6-Dichloro-2,3-dimethylphenol  
 3:2216 2,5-Dichloro-3,4-dimethylphenol  
 3:0935 2,6-Dichloro-3,4-dimethylphenol



3:3005	5,6-Dichloro-3,4-dimethylphenol	3:2637	3,5-Dichloro-2-hydroxybenzaldehyde
3:2182	2,4-Dichloro-3,5-dimethylphenol	3:4140	2,4-Dichloro-3-hydroxybenzaldehyde
3:2638	2,6-Dichloro-3,5-dimethylphenol	3:4160	2,6-Dichloro-3-hydroxybenzaldehyde
3:2570	<i>d,t</i> -1,2-Dichloro-1,2-diphenylethane	3:3952	4,6-Dichloro-3-hydroxybenzaldehyde
3:4854	<i>meso</i> -1,2-Dichloro-1,2-diphenylethane	3:4100	3,5-Dichloro-4-hydroxybenzaldehyde
3:1940	1,1-Dichloro-2,2-diphenylethane	3:4935	3,5-Dichloro-2-hydroxybenzoic acid
3:1380	<i>cis</i> -1,2-Dichloro-1,2-diphenylethylene	3:4950	3,5-Dichloro-4-hydroxybenzoic acid
3:4210	<i>trans</i> -1,2-Dichloro-1,2-diphenylethylene	3:2145	$\beta,\beta$ -Dichloro- $\alpha$ -hydroxyisobutyric acid
3:1938	1,1-Dichloro-2,2-diphenylethylene	3:2565	$\beta,\beta'$ -Dichloro- $\alpha$ -hydroxyisobutyric acid
3:1057	4,4'-Dichlorodiphenylmethane	3:5300	$\alpha,\alpha$ -Dichloroisobutylene
3:6960	$\alpha,\alpha$ -Dichlorodiphenylmethane	3:5590	$\alpha,\gamma$ -Dichloroisobutylene
3:8610	$\beta,\beta'$ -Dichloro- <i>di-n</i> -propyl ether	3:5633	$\gamma,\gamma'$ -Dichloroisobutylene
3:8745	$\gamma,\gamma'$ -Dichloro- <i>di-n</i> -propyl ether	3:4965	4,6-Dichloroisophthalic acid
3:6960	$\alpha,\alpha$ -Dichloroditan	3:6318	$\beta,\beta'$ -Dichloroisopropyl acetate
3:5035	1,1-Dichloroethane	3:5755	$\beta,\beta$ -Dichloroisopropyl alcohol
3:5130	1,2-Dichloroethane	3:5985	$\beta,\beta'$ -Dichloroisopropyl alcohol
3:5130	<i>sym.</i> -Dichloroethane	3:9394	$\beta,\beta'$ -Dichloroisopropyl-ethylformal
3:5035	<i>unsym.</i> -Dichloroethane	3:3634	Dichloromaleic acid
3:5745	2,2-Dichloroethanol-1	3:3635	Dichloromaleic anhydride
3:5540	$\alpha,\beta$ -Dichloro- $\alpha$ -ethoxyethylene	3:6197	Dichloromaleyl (di)chloride
3:5745	$\beta,\beta$ -Dichloroethyl alcohol	3:5020	Dichloromethane
3:6655	$\alpha,\beta$ -Dichloroethylbenzene	3:7920	1,2-Dichloro-2-methylbutane
3:6790	Di( $\beta$ -chloroethyl) carbonate	3:9223	1,3-Dichloro-2-methylbutane
3:6790	$\beta,\beta$ -Dichloroethyl carbonate	3:8360	1,4-Dichloro-2-methylbutane
3:5005	1,1-Dichloroethylene	3:7975	2,3-Dichloro-2-methylbutane
3:5030	1,2-Dichloroethylene (ordinary mixt.)	3:8105	2,4-Dichloro-2-methylbutane
3:5005	<i>unsym.</i> -Dichloroethylene	3:9230	3,3-Dichloro-2-methylbutane
3:5042	<i>cis</i> -1,2-Dichloroethylene	3:8075	3,4-Dichloro-2-methylbutane
3:5028	<i>trans</i> -1,2-Dichloroethylene	3:7885	4,4-Dichloro-2-methylbutane
3:5640	$\alpha,\beta$ -Dichloroethyl ethyl ether	3:7690	3,3-Dichloro-2-methylbutene-1
3:9534	1,3-Dichloro-2-ethylhexane	3:8170	1,3-Dichloro-2-methylbutene-2
3:0572	Di( $\beta$ -chloroethyl) oxalate	3:9204	1,4-Dichloro-2-methylbutene-2
3:5010	1,2-Dichloroethyne	3:5315	Dichloromethyl chlorocarbonate
3:8650	1,1-Dichloroheptane	3:5315	Dichloromethyl chloroformate
3:9420	1,2-Dichloroheptane	3:5772	Dichloromethyl-dimethylcarbinol
3:9422	1,7-Dichloroheptane	3:5755	Dichloromethyl-methylcarbinol
3:9424	2,2-Dichloroheptane	3:5430	Dichloromethyl methyl ketone
3:9426	4,4-Dichloroheptane	3:9346	2,3-Dichloro-2-methylpentane
3:9310	1,3-Dichlorohexadiene-2,4	3:8550	2,5-Dichloro-2-methylpentane
3:8380	1,2-Dichlorohexane	3:2910	4,5-Dichloro-2-methylphenol
3:9340	1,5-Dichlorohexane	3:1020	4,6-Dichloro-2-methylphenol
3:8720	1,6-Dichlorohexane	3:1205	2,4-Dichloro-3-methylphenol
3:9342	2,2-Dichlorohexane	3:0150	2,6-Dichloro-3-methylphenol
3:8300	2,3-Dichlorohexane	3:1745	4,6-Dichloro-3-methylphenol
3:8525	2,5-Dichlorohexane	3:0400	2,6-Dichloro-4-methylphenol
3:9344	3,4-Dichlorohexane	3:7425	1,1-Dichloro-2-methylpropane
3:9300	3,4-Dichlorohexatriene-1,2,4,5	3:7430	1,2-Dichloro-2-methylpropane
3:9304	3,6-Dichlorohexatriene-1,3,4	3:7960	1,3-Dichloro-2-methylpropane
3:9330	1,2-Dichlorohexene-1	3:5772	1,1-Dichloro-2-methylpropanol-2
3:5935	" $\alpha$ -Dichlorohydrin "	3:5977	1,3-Dichloro-2-methylpropanol-2
3:5060	" $\beta$ -Dichlorohydrin "	3:5300	1,1-Dichloro-2-methylpropene-1
3:4220	2,3-Dichlorohydroquinone	3:5590	1,3-Dichloro-2-methylpropene-1
3:4600	2,5-Dichlorohydroquinone		
3:4600	2,6-Dichlorohydroquinone		
3:4220	<i>o</i> -Dichlorohydroquinone		
3:4600	<i>m</i> -Dichlorohydroquinone		
3:4690	<i>p</i> -Dichlorohydroquinone		

- 3:7480 3,3-Dichloro-2-methylpropene-1  
 3:7480 1,1-Dichloro-2-methylpropene-2  
 3:0320 1,2-Dichloronaphthalene  
 3:1310 1,3-Dichloronaphthalene  
 3:1655 1,4-Dichloronaphthalene  
 3:3200 1,5-Dichloronaphthalene  
 3:0810 1,6-Dichloronaphthalene  
 3:1385 1,7-Dichloronaphthalene  
 3:2435 1,8-Dichloronaphthalene  
 3:3665 2,3-Dichloronaphthalene  
 3:0810 2,5-Dichloronaphthalene  
 3:4040 2,6-Dichloronaphthalene  
 3:3445 2,7-Dichloronaphthalene  
 3:1385 2,8-Dichloronaphthalene  
 3:2935 2,3-Dichloronaphthol-1  
 3:3250 2,4-Dichloronaphthol-1  
 3:3985 5,7-Dichloronaphthol-1  
 3:3420 5,8-Dichloronaphthol-1  
 3:4315 6,7-Dichloronaphthol-1  
 3:2635 7,8-Dichloronaphthol-1  
 3:1990 1,3-Dichloronaphthol-2  
 3:3840 1,4-Dichloronaphthol-2  
 3:3600 1,6-Dichloronaphthol-2  
 3:3295 3,4-Dichloronaphthol-2  
 3:4420 4,8-Dichloronaphthol-2  
 3:4155 5,8-Dichloronaphthol-2  
 3:4857 2,3-Dichloronaphthoquinone-1,4  
 3:4775 3,4-Dichloronaphthoquinone-1,2  
 3:0632 1,2-Dichlorononane  
 3:8880 1,6-Dichlorononane  
 3:0530 1,6-Dichlorooctane  
 3:0532 1,7-Dichlorooctane  
 3:8805 1,8-Dichlorooctane  
 3:8670 2,2-Dichlorooctane  
 3:8015 1,1-Dichloropentane  
 3:8140 1,2-Dichloropentane  
 3:9220 1,3-Dichloropentane  
 3:9224 1,4-Dichloropentane  
 3:8575 1,5-Dichloropentane  
 3:7755 2,2-Dichloropentane  
 3:8010 2,3-Dichloropentane  
 3:8120 2,4-Dichloropentane  
 3:7895 3,3-Dichloropentane  
 3:8045 3,4-Dichloropentane-2  
 3:9202 2,5-Dichloropentane-2  
 3:1175 2,3-Dichlorophenol  
 3:0560 2,4-Dichlorophenol  
 3:1190 2,5-Dichlorophenol  
 3:1595 2,6-Dichlorophenol  
 3:1460 3,4-Dichlorophenol  
 3:1670 3,5-Dichlorophenol  
 3:4095 2,4-Dichlorophenoxyacetic acid  
 3:4612 Di-(*p*-chlorophenyl)acetic acid  
 3:6685 1,2-Dichloro-1-phenylethane  
 3:0995 1,1-Di-(*p*-chlorophenyl)ethane  
 3:2475 1,1-Di-(*p*-chlorophenyl)ethylene  
 3:0717 Di-(*o*-chlorophenyl) ketone  
 3:3860 Di-(*m*-chlorophenyl) ketone  
 3:4270 Di-(*p*-chlorophenyl) ketone  
 3:1057 Di-(*p*-chlorophenyl)methane  
 3:0825 2,4-Dichlorophenyl phenyl ketone  
 3:2340 2,5-Dichlorophenyl phenyl ketone  
 3:2285 2,6-Dichlorophenyl phenyl ketone  
 3:3070 3,4-Dichlorophenyl phenyl ketone  
 3:1505 3,5-Dichlorophenyl phenyl ketone  
 3:4880 3,4-Dichlorophthalic acid  
 3:4580 3,5-Dichlorophthalic acid  
 3:4870 3,6-Dichlorophthalic acid  
 3:4890 4,5-Dichlorophthalic acid  
 3:3625 3,4-Dichlorophthalic anhydride  
 3:2375 3,5-Dichlorophthalic anhydride  
 3:4860 3,6-Dichlorophthalic anhydride  
 3:4830 4,5-Dichlorophthalic anhydride  
 3:2395 3,3-Dichlorophthalide  
 3:9033-A 2,2-Dichloropropanal-1  
 3:9034 2,3-Dichloropropanal-1  
 3:7230 1,1-Dichloropropane  
 3:5200 1,2-Dichloropropane  
 3:5450 1,3-Dichloropropane  
 3:7140 2,2-Dichloropropane  
 3:6060 2,3-Dichloropropanol-1  
 3:5755 1,1-Dichloropropanol-2  
 3:5985 1,3-Dichloropropanol-2  
 3:5430 1,1-Dichloropropanone-2  
 3:0563 1,3-Dichloropropanone-2  
 3:5120 1,1-Dichloropropene-1  
 3:5150 1,2-Dichloropropene-1 (*h*-b. isomer)  
 3:5110 1,2-Dichloropropene-1 (*l*-b. isomer)  
 3:5290 1,3-Dichloropropene-1  
 3:5100 2,3-Dichloropropene-1  
 3:5140 3,3-Dichloropropene-1  
 3:5140 1,1-Dichloropropene-2  
 3:9033-A  $\alpha,\alpha$ -Dichloropropionaldehyde  
 3:9034  $\alpha,\beta$ -Dichloropropionaldehyde  
 3:6162  $\alpha,\alpha$ -Dichloropropionic acid  
 3:0855  $\alpha,\beta$ -Dichloropropionic acid  
 3:1058  $\beta,\beta$ -Dichloropropionic acid  
 3:5372  $\alpha,\alpha$ -Dichloropropionyl chloride  
 3:9032  $\alpha,\beta$ -Dichloropropionyl chloride  
 3:9032-A  $\beta,\beta$ -Dichloropropionyl chloride  
 3:6220  $\beta,\gamma$ -Dichloro-*n*-propyl acetate  
 3:6895 Di-(*γ*-chloropropyl) carbonate  
 3:6895  $\gamma,\gamma'$ -Dichloropropyl carbonate  
 3:5280  $\alpha,\gamma$ -Dichloropropylene  
 3:2192 3,5-Dichloropyrocatechol  
 3:3525 4,5-Dichloropyrocatechol  
 3:4220 2,3-Dichloroquinol  
 3:3390 4,6-Dichlororesorcinol  
 3:2637 3,5-Dichlorosalicylaldehyde  
 3:4935 3,5-Dichlorosalicylic acid  
 3:1380 *cis*- $\alpha,\alpha'$ -Dichlorostilbene  
 3:4210 *trans*- $\alpha,\alpha'$ -Dichlorostilbene  
 3:4711 *d,l*- $\alpha,\alpha'$ -Dichlorosuccinic acid  
 3:4930 *meso*- $\alpha,\alpha'$ -Dichlorosuccinic acid  
 3:4711 *allo*-Dichlorosuccinic acid  
 3:0395 *d,l*- $\alpha,\alpha'$ -Dichlorosuccinyl (di)-chloride  
 3:9087 *meso*- $\alpha,\alpha'$ -Dichlorosuccinyl (di)-chloride

3:4985	2,5-Dichloroterephthalic acid	3:7900	Dimethyl-ethyl-acetyl chloride
3:6327	$\alpha,\alpha$ -Dichlorotoluene	3:7220	Dimethyl-ethyl-carbinyl chloride
3:6327	$\omega,\omega$ -Dichlorotoluene	3:9287	Dimethyl-ethyl-carbinyl hypochlorite
3:6345	2,3-Dichlorotoluene		
3:6290	2,4-Dichlorotoluene	3:7752	$\alpha,\alpha$ -Dimethylethylene $\alpha$ -chlorohydrin
3:6245	2,5-Dichlorotoluene		
3:6270	2,6-Dichlorotoluene	3:7750	Dimethyl-isohutyl-carbinyl chloride
3:6355	3,4-Dichlorotoluene		
3:6310	3,5-Dichlorotoluene	3:0485	Dimethyl isodichlorosuccinate
3:9536	3,3-Dichloro-2,2,4-trimethylpentane	3:8145	Dimethyl-isopropyl-acetyl chloride
3:5540	$\alpha,\beta$ -Dichlorovinyl ethyl ether	3:7600	Dimethyl-isopropyl-carbinyl chloride
3:1040	$\omega,\omega'$ -Dichloro- <i>o</i> -xylene		
3:0310	$\omega,\omega'$ -Dichloro- <i>m</i> -xylene	3:1355	2,4-Dimethylphenacyl chloride
3:2825	$\omega,\omega'$ -Dichloro- <i>p</i> -xylene	3:0245	2,5-Dimethylphenacyl chloride
3:2442	4,5-Dichloro- <i>o</i> -3-xyleneol	3:1775	3,4-Dimethylphenacyl chloride
3:0935	3,5-Dichloro- <i>o</i> -4-xyleneol	3:9610	Dimethyl-phenyl-carbinyl chloride
3:2216	3,6-Dichloro- <i>o</i> -4-xyleneol		
3:3005	5,6-Dichloro- <i>o</i> -4-xyleneol	3:7450	$\alpha,\alpha$ -Dimethylpropionyl chloride
3:2182	2,4-Dichloro- <i>m</i> -5-xyleneol	3:9456	Dimethyl- <i>n</i> -propyl-acetyl chloride
3:2638	2,6-Dichloro- <i>m</i> -5-xyleneol		
3:7990	Diethylacetyl chloride	3:7490	Dimethyl- <i>n</i> -propyl-carbinyl chloride
3:7330	Diethylcarbinyl chloride		
3:6864	Diethyl chlorofumarate	3:9456	$\alpha,\alpha$ -Dimethyl- <i>n</i> -valeryl chloride
3:6697	Diethyl chloromaleate	3:9458	$\alpha,\beta$ -Dimethyl- <i>n</i> -valeryl chloride
3:9578	Diethyl <i>d,l</i> - $\alpha,\alpha'$ -dichlorosuccinate	3:9460	$\gamma,\gamma$ -Dimethyl- <i>n</i> -valeryl chloride
		3:7120	$\beta,\beta$ -Dimethylvinyl chloride
3:9578	Diethyl <i>allo</i> -dichlorosuccinate	3:9402	Dimethyl-vinylethynyl-carbinyl chloride
3:1364	Diethyl <i>meso</i> - $\alpha,\alpha'$ -dichlorosuccinate		
		3:0060	Diphenylcarbinyl chloride
3:9390	Diethylene glycol mono(chloroacetate)	3:3585	Diphenylchloroacetio acid
		3:0885	Diphenyl-chloro-acetyl chloride
3:9185	Diethylene glycol chlorohydrin	3:0060	Diphenyl-chloromethane
3:0578	Diethyl isodichlorosuccinate	3:9870	1,1-Diphenylethyl chloride
3:8210	Diethyl-isopropyl-carbinyl chloride	3:9871	2,2-Diphenylethyl chloride
		3:0060	Diphenylmethyl chloride
3:7585	Diethyl-methyl-carbinyl chloride	3:5515	"Diphosgene"
		3:8095	Di- <i>n</i> -propyl-carbinyl chloride
3:8223	Diethyl- <i>n</i> -propyl-carbinyl chloride	3:1915	Di-(trichloromethyl) carbonate
		3:6373	Di-(trichlorovinyl) ether
3:9092	Diglycolyl dichloride	3:9310	Divinylacetylene dihydrochloride
3:9039	$\beta,\beta'$ -Dihydroxyisopropyl chloride	3:9858	<i>n</i> -Dodecanoyl chloride
3:8113	Di-isohutylene hydrochloride	3:8810	<i>n</i> -Dodecyl chloride
3:9744	Di-isohutyl-methyl-carbinyl chloride		
3:9527	Di-isocrotyl hydrochloride		
3:1550	Di-isocrotyl bis-hydrochloride	3:0950	Elaidyl chloride
3:9240	<i>cis</i> - $\alpha,\beta$ -Dimethyl-acryloyl chloride	3:8520	Enanthoyl chloride
		3:5358	"Epichlorohydrin"
3:7300	$\alpha,\beta$ -Dimethylallyl chloride	3:9082	Erythrene tetrachloride (liquid isomer)
3:7400	$\alpha,\gamma$ -Dimethylallyl chloride		
3:7485	$\beta,\gamma$ -Dimethylallyl chloride	3:1760	Erythrene tetrachloride (solid isomer)
3:7465	$\gamma,\gamma$ -Dimethylallyl chloride		
3:7900	$\alpha,\alpha$ -Dimethyl- <i>n</i> -hutryl chloride	3:7065	Ethanoyl chloride
3:7965	$\alpha,\beta$ -Dimethyl- <i>n</i> -hutryl chloride	3:5625	Ethoxalyl chloride
3:7880	$\beta,\beta$ -Dimethyl- <i>n</i> -hutryl chloride	3:7745	Ethoxyacetyl chloride
3:6582	Dimethyl chlorofumarate	3:7305	$\alpha$ -Ethoxyethyl chloride
3:9251	Dimethyl chloromaleate	3:7463	$\beta$ -Ethoxyethyl chloride
3:0485	Dimethyl <i>d,l</i> - $\alpha,\alpha'$ -dichlorosuccinate	3:9280	$\beta$ -Ethoxyethyl chlorocarbonate
		3:9280	$\beta$ -Ethoxyethyl chloroformate
3:0485	Dimethyl <i>allo</i> -dichlorosuccinate	3:7260	$\alpha$ -Ethylallyl chloride
3:0240	Dimethyl <i>meso</i> - $\alpha,\alpha'$ -dichlorosuccinate	3:9214	$\beta$ -Ethylallyl chloride
		3:7470	$\gamma$ -Ethylallyl chloride

## E

3:8080	Ethyl- <i>n</i> -butyl-carbinyl chloride	3:9462	$\alpha$ -Ethyl-isovaleryl chloride
3:7720	2-Ethylbutyl chloride	3:7603	Ethyl-methyl-acetyl chloride
3:7990	$\alpha$ -Ethyl- <i>n</i> -butyryl chloride	3:7660	$\alpha$ -Ethyl- $\beta$ -methylallyl chloride
3:7015	Ethyl chloride	3:7675	$\alpha$ -Ethyl- $\gamma$ -methylallyl chloride
3:5700	Ethyl chloroacetate	3:9462	$\alpha$ -Ethyl- $\beta$ -methyl- <i>n</i> -butyryl chloride
3:6207	Ethyl $\alpha$ -chloroacetoacetate	3:7125	Ethyl-methyl-carbinyl chloride
3:6375	Ethyl $\gamma$ -chloroacetoacetate	3:8175	<i>unsym.</i> -Ethyl-methyl-ethylene chlorohydrin
3:9242	Ethyl $\alpha$ -chloroacrylate	3:8010	<i>sym.</i> -Ethyl-methyl-ethylene dichloride
3:6800	Ethyl $\alpha$ -chlorobenzoate	3:7950	Ethyl-methyl- <i>n</i> -propyl-carbinyl chloride
3:6770	Ethyl <i>m</i> -chlorobenzoate	3:8235	Ethyl- <i>n</i> -propyl-acetyl chloride
3:6750	Ethyl <i>p</i> -chlorobenzoate	3:7670	Ethyl- <i>n</i> -propyl-carbinyl chloride
3:8307	Ethyl $\alpha$ -chloro- <i>n</i> -butyrate	3:5950	Ethyl trichloroacetate
3:8373	Ethyl $\beta$ -chloro- <i>n</i> -butyrate	3:6380	Ethyl $\alpha, \alpha, \beta$ -trichloro- <i>n</i> -butyrate
3:8597	Ethyl $\gamma$ -chloro- <i>n</i> -butyrate	3:5955	Ethyl-trichloromethyl-carbinol
3:7295	" Ethyl chlorocarbonate "	3:8235	$\alpha$ -Ethyl- <i>n</i> -valeryl chloride
3:8523	Ethyl $\alpha$ -chlorocrotonate		
3:8538	Ethyl $\beta$ -chlorocrotonate		
3:8657	Ethyl $\gamma$ -chlorocrotonate		
3:5270	" Ethyl chloroform "		
3:7295	Ethyl chloroformate		
3:9246	Ethyl (chloroformyl)acetate		
3:8147	Ethyl $\alpha$ -chloro-isobutyrate	3:9394	Formaldehyde $\beta, \beta'$ -dichloro-isopropyl-ethyl-acetal
3:9368	Ethyl $\alpha$ -chloroisocrotonate	3:5975	Fumaryl (di)chloride
3:8325	Ethyl $\beta$ -chloroisocrotonate	3:8515	Furan 2-carboxylic acid chloride
3:8528	Ethyl $\alpha$ -chloro-isovalerate	3:8515	Furoyl chloride
3:6207	Ethyl $\alpha$ -chloro- $\beta$ -keto- <i>n</i> -butyrate		
3:6375	Ethyl $\gamma$ -chloro- $\beta$ -keto- <i>n</i> -butyrate		
3:8518	Ethyl $\alpha$ -chloro- $\alpha$ -methyl- <i>n</i> -butyrate		
3:8528	Ethyl $\alpha$ -chloro- $\beta$ -methyl- <i>n</i> -butyrate	3:6500	Glutaryl (di)chloride
3:8125	Ethyl $\alpha$ -chloropropionate	3:6775	Glycerol $\alpha$ -chlorohydrin $\alpha'$ -acetate
3:8290	Ethyl $\beta$ -chloropropionate	3:6517	Glycerol $\alpha$ -chlorohydrin $\beta$ -acetate
3:8596	Ethyl $\alpha$ -chloro- <i>n</i> -valerate	3:6648	Glycerol $\beta$ -chlorohydrin $\alpha$ -acetate
3:8629	Ethyl $\beta$ -chloro- <i>n</i> -valerate	3:5985	Glycerol $\alpha, \alpha'$ -dichlorohydrin
3:8703	Ethyl $\gamma$ -chloro- <i>n</i> -valerate	3:6060	Glycerol $\alpha, \beta$ -dichlorohydrin
3:8727	Ethyl $\delta$ -chloro- <i>n</i> -valerate	3:6318	Glycerol $\alpha, \alpha'$ -dichlorohydrin $\beta$ -acetate
3:7675	$\alpha$ -Ethylcrotyl chloride	3:6220	Glycerol $\alpha$ - $\beta$ -dichlorohydrin $\alpha'$ -acetate
3:5850	Ethyl dichloroacetate	3:9038	Glycerol $\alpha$ -monochlorohydrin
3:6090	Ethyl $\alpha, \beta$ -dichloropropionate	3:9039	Glycerol $\beta$ -monochlorohydrin
3:9648	Ethyl-di- <i>n</i> -propyl-carbinyl chloride	3:6840	Glycerol $\alpha$ -monochlorohydrin diacetate
3:5130	Ethylene (di)chloride	3:5840	Glycerol trichlorohydrin
3:5552	Ethylene chlorohydrin	3:5552	" Glycol chlorohydrin "
3:6780	Ethylene glycol mono(chloro-acetate)		
3:0720	Ethylene glycol bis-(chloro-acetate)		
3:9185	Ethylene glycol mono-( $\beta$ -chloroethyl) ether	3:9800	<i>n</i> -Hendecanoyl chloride
3:6655	Ethylene glycol bis-( $\beta$ -chloro-ethyl) ether	3:9800	<i>n</i> -Hendecoyl chloride
3:9322	Ethyl-ethynyl-methyl-carbinyl chloride	3:9056	1,1,2,2,3,4,4-Heptachlorobutane
3:8370	2-Ethylhexyl chloride	3:6860	<i>sym.</i> -Heptachloropropane
3:7022	Ethyl hypochlorite	3:0200	<i>unsym.</i> -Heptachloropropane
3:5035	Ethylidene (di)chloride	3:0200	1,1,1,2,2,3,3-Heptachloropropane
3:9652	Ethyl-isoamyl-methyl-carbinyl chloride	3:6860	1,1,1,2,3,3,3-Heptachloropropane
3:9462	Ethyl-isopropyl-acetyl chloride	3:9925	<i>n</i> -Heptadecanoyl chloride
3:7565	Ethyl-isopropyl-carbinyl chloride	3:0100	<i>n</i> -Heptadecyl chloride
3:7970	Ethyl-isopropyl-methyl-carbinyl chloride	3:9122	Heptamethylene dichloride
		3:8520	<i>n</i> -Heptanoyl chloride
		3:8250	<i>n</i> -Heptyl chloride
		3:8635	<i>n</i> -Heptyl-methyl-carbinyl chloride

3:6312	Hexachloroacetone	3:8215	Isoamyl chlorocarbonate
3:4939	Hexachlorobenzene	3:8215	Isoamyl chloroformate
3:6425	Hexachlorobutadiene-1,3	3:9580	Isoamyl $\alpha$ -chloropropionate
3:3165	1,1,2,3,4,4-Hexachlorobutane	3:8730	Isoamyl $\beta$ -chloropropionate
3:1945	1,1,2,3,4,4-Hexachlorobutene-2 (solid isomer)	3:9555	Isoamyl-dimethyl-carbinyl chloride
3:9045	1,1,2,3,4,4-Hexachlorobutene-2 (liquid isomer)	3:7955	Isoamyl-methyl-carbinyl chloride
3:9048	Hexachlorobutene-X	3:9628	Isoamyl-propenyl-carbinyl chloride
3:9050	Hexachlorobutene-Y	3:6490	Isoamyl trichloroacetate
3:3180	Hexachlorocyclohexadien-2,5- one-1	3:7145	Isobutenyl chloride
3:4410	cis-1,2,3,4,5,6-Hexachlorocyclo- hexane	3:8090	Isobutyl-acetyl chloride
3:4990	trans-1,2,3,4,5,6-Hexachloro- cyclohexane	3:7135	Isobutyl chloride
3:3470	1,2,4,4,6,6-Hexachlorocyclo- hexen-1-dione-3,5	3:8375	Isobutyl chloroacetate
3:2360	2,3,5,5,6,6-Hexachlorocyclo- hexen-5-dione-1,4	3:7760	Isobutyl chlorocarbonate
3:1915	Hexachlorodimethyl carbonata	3:9215	" Isobutylchloroform "
3:4835	Hexachloroethane	3:7760	Isobutyl chloroformate
3:1220	1,2,3,4,5,6-Hexachlorohexene-3	3:9470	Isobutyl $\alpha$ -chloropropionate
3:3180	" Hexachlorophenol "	3:8655	Isobutyl $\beta$ -chloropropionate
3:6460	1,1,1,2,3,3-Hexachloropropane	3:7752	Isobutylene $\alpha$ -chlorohydrin
3:6525	1,1,2,2,3,3-Hexachloropropane	3:7905	" $\beta$ -Isobutylene chlorohydrin "
3:6525	sym.-Hexachloropropane	3:7430	Isobutylene dichloride
3:6460	unsym.-Hexachloropropane	3:7425	Isobutylidene (di)chloride
3:6312	Hexachloropropanone-2	3:7495	Isobutyl-methyl-carbinyl chloride
3:6370	Hexachloropropene	3:6140	Isobutyl trichloroacetate
3:3470	" Hexachlororesorcinol "	3:7270	Isobutyryl chloride
3:9912	n-Hexadecanoyl chloride	3:8090	Isocaproyl chlorida
3:0015	n-Hexadecyl chloride	3:1903	Isocrotonic acid dichlorida
3:8580	Hexahydrobenzoyl chloride	3:7120	Isocrotyl chlorida
3:8720	Hexamethylene dichloride	3:4711	Isodichlorosuccinic acid
3:8168	n-Hexanoyl chloride	3:9750	$\beta$ -Isoduryl chloride
3:7955	n-Hexyl chloride	3:8365	Isheptanoyl chloride
3:7715	sec-(2)-Hexyl chloride	3:7695	Isohexyl chlorida
3:7670	sec-(3)-Hexyl chloride	3:9540	Isohexyl-methyl-carbinyl chlorida
3:8378	n-Hexyl-methyl-carbinyl chlorida	3:0520	Isophthaloyl (di)chloride
3:8787	Hydrocinnamoyl chloride	3:0520	Isophthalyl (di)chlorida
3:8777	Hydrocinnamyl chloride	3:0846	" Isopral "
3:0085	2-Hydroxybenzoyl chloride	3:8105	Isoprene $\delta$ s-hydrochloride
3:9445	3-Hydroxybenzoyl chloride	3:7465	Isoprene hydrochloride
3:9447	4-Hydroxybenzoyl chloride	3:9200	" Isoprene monochloride "
3:9107	2-Hydroxy-2-(dichloromethyl)- 1,3-dioxolane	3:7920	Isopropenyl chloride
3:9588	$\beta$ -[( $\beta$ -Hydroxyethoxy)ethoxy]- ethyl chloroacetate	3:7358	Isopropenyl chlorocarbonate
3:9390	$\beta$ -( $\beta$ -Hydroxyethoxy)ethyl chloroacetate	3:7358	Isopropenyl chloroformate
3:6780	$\beta$ -Hydroxyethyl chloroacetate	3:8795	4-Isopropylbenzyl chloride
3:9107	$\beta$ -Hydroxyethyl dichloroacetate	3:7135	Isopropylcarbinyl chloride
3:9099	$\beta$ -Hydroxyethyl trichloroacetate	3:7025	Isopropyl chlorida
3:9570	$\beta$ -Hydroxy- $\beta$ -phenyl-ethyl chlo- ride	3:8160	Isopropyl chloroacetate
3:9099	2-Hydroxy-2-(trichloromethyl)- 1,3-dioxolane	3:7405	Isopropyl chlorocarbonate
	I	3:7495	Isopropyl chloroformate
3:8365	Isoamylacetyl chloride	3:8165	Isopropyl $\alpha$ -chloropropionate
3:7365	Isoamyl chloride	3:9388	Isopropyl $\beta$ -chloropropionate
3:7275	sec.-Isoamyl chloride	3:5890	Isopropyl dichloroacetate
		3:8075	Isopropylethylene dichloride
		3:7140	Isopropylidene (di)chloride
		3:7965	Isopropyl-methyl-acetyl chloride
		3:7275	Isopropyl-methyl-carbinyl chlo- ride
		3:9554	Isopropyl-methyl-n-propyl- carbinyl chloride
		3:5975	Isopropyl trichloroacetate
		3:7560	Isovaleryl chloride

K			
3:9098	$\beta$ -Keto- <i>n</i> -butyryl chloride	3:9792	Methyl $\omega$ -(chloroformyl)-pelargonato
L		3:9247	Methyl $\beta$ -(chloroformyl)-propionate
3:9858	<i>n</i> -Lauroyl chloride	3:7918	Methyl $\alpha$ -chloroisobutyrate
3:8810	<i>n</i> -Lauryl chloride	3:8028	Methyl $\beta$ -chloroisocrotonate
M		3:7360	"Methylchloroprene"
3:9030	Malonyl dichloride	3:7908	Methyl $\alpha$ -chloropropionate
3:9925	<i>n</i> -Margaroyl chloride	3:5765	Methyl $\beta$ -chloropropionate
3:0250	$\alpha$ -Menaphthyl chloride	3:8264	Methyl $\alpha$ -chloro- <i>n</i> -valerate
3:0747	$\beta$ -Menaphthyl chloride	3:9240	<i>cis</i> - $\alpha$ -Methylcrotonoyl chloride
3:9750	Mesityl chloride	3:7400	$\alpha$ -Methylcrotyl chloride
3:7145	Methallyl chloride	3:5655	Methyl dichloroacetate
3:5225	Methoxyacetyl chloride	3:9103	Methyl $\alpha,\beta$ -dichloropropionate
3:6870	2-Methoxybenzoyl chloride	3:9550	Methyl-di- <i>n</i> -propyl-carbinyl chloride
3:6797	3-Methoxybenzoyl chloride	3:5020	Methylene ( <i>di</i> )chloride
3:6890	4-Methoxybenzoyl chloride	3:1960	3,4-Methylenedioxybenzoyl chloride
3:7150	$\alpha$ -Methoxyethyl chloride	3:7657	" $\beta$ -Methylepicchlorohydrin"
3:7265	$\beta$ -Methoxyethyl chloride	3:9190	$\beta$ -Methylglycerol $\alpha$ -monochlorohydrin
3:9255	$\beta$ -Methoxyethyl chloroacetate	3:9140	Methyl-neopentyl-carbinyl chloride
3:9140	$\beta$ -Methoxyethyl chlorocarbonate	3:9660	<i>o</i> -Methylphenacyl chloride
3:9250	$\beta$ -Methoxyethyl trichloroacetate	3:1130	<i>p</i> -Methylphenacyl chloride
3:7085	Methoxymethyl chloride	3:8667	Methyl-phenyl-carbinyl chloride
3:7090	$\alpha$ -Methylallyl chloride	3:7175	$\gamma$ -Methylpropargyl chloride
3:7145	$\beta$ -Methylallyl chloride	3:8020	Methyl- <i>n</i> -propyl-acetyl chloride
3:7205	$\gamma$ -Methylallyl chloride	3:7325	Methyl- <i>n</i> -propyl-carbinyl chloride
3:8740	<i>o</i> -Methylbenzoyl chloride	3:5800	Methyl trichloroacetate
3:6535	<i>m</i> -Methylbenzoyl chloride	3:6620	Methyl trichloromethyl ketone
3:6600	<i>p</i> -Methylbenzoyl chloride	3:9020	$\alpha$ -Methyl- <i>n</i> -valeryl chloride
3:8710	<i>o</i> -Methylbenzyl chloride	3:8035	$\beta$ -Methyl- <i>n</i> -valeryl chloride
3:8700	<i>m</i> -Methylbenzyl chloride	3:8090	$\gamma$ -Methyl- <i>n</i> -valeryl chloride
3:8660	<i>p</i> -Methylbenzyl chloride	3:7020	$\alpha$ -Methylvinyl chloride
3:7603	$\alpha$ -Methyl- <i>n</i> -butyryl chloride	3:7030	$\beta$ -Methylvinyl chloride
3:7560	$\beta$ -Methyl- <i>n</i> -butyryl chloride	3:9038	" $\alpha$ -Monochlorohydrin"
3:9452	$\alpha$ -Methyl- <i>n</i> -caproyl chloride	3:9039	" $\beta$ -Monochlorohydrin"
3:8305	$\beta$ -Methyl- <i>n</i> -caproyl chloride	3:6840	" $\alpha$ -Monochlorohydrin" diacetate
3:8355	$\gamma$ -Methyl- <i>n</i> -caproyl chloride	3:9885	<i>n</i> -Myristoyl chloride
3:8365	$\delta$ -Methyl- <i>n</i> -caproyl chloride	3:9674	<i>n</i> -Myristyl chloride
3:9285	"Methylcellosolve" chloroacetate		
3:9140	"Methylcellosolve" chloroformate		
3:9250	"Methylcellosolve" trichloroacetate		
N			
3:7005	Methyl chloride	3:4750	Napthalene tetrachloride
3:5585	Methyl chloroacetate	3:6930	$\alpha$ -Naphthoyl chloride
3:9096	Methyl $\alpha$ -chloroacrylate	3:0900	$\beta$ -Naphthoyl chloride
3:6695	Methyl <i>o</i> -chlorobenzoate	3:9856	$\alpha$ -Naphthylacetyl chloride
3:6670	Methyl <i>m</i> -chlorobenzoate	3:0250	$\alpha$ -Naphthylmethyl chloride
3:0535	Methyl <i>p</i> -chlorobenzoate	3:0747	$\beta$ -Naphthylmethyl chloride
3:8103	Methyl $\alpha$ -chloro- <i>n</i> -butyrate	3:7590	Neohexyl chloride
3:8224	Methyl $\beta$ -chloro- <i>n</i> -butyrate	3:9160	Neopentylacetyl chloride
3:8517	Methyl $\gamma$ -chloro- <i>n</i> -butyrate	3:7555	Neopentylcarbinyl chloride
3:5075	"Methyl chlorocarbonate"	3:7200	Neopentyl chloride
3:5870	Methyl $\alpha$ -chlorocrotonate	3:8780	Neophyl chloride
3:9244	Methyl $\beta$ -chlorocrotonate	3:8765	<i>n</i> -Nonanoyl chloride
3:5085	Methyl chloroform	3:8719	<i>n</i> -Nonyl chloride
3:5075	Methyl chloroformate		
3:9098-A	Methyl (chloroformyl)acetate		
3:9373	Methyl $\gamma$ -(chloroformyl)- <i>n</i> -butyrate	3:2000	1,1,2,2,3,3,4,4-Octachlorobutane
		3:0122	Octachlorocyclopentene

3:0843	Trichloroacetaldehyde <i>n</i> -butylhemiacetal	3:9094	$\alpha,\alpha,\gamma$ -Trichloro- <i>n</i> -butyraldehyde
3:6317	Trichloroacetaldehyde diethylacetal	3:1905	$\alpha,\alpha,\beta$ -Trichloro- <i>n</i> -butyraldehyde hydrate
3:0860	Trichloroacetaldehyde (mono)-ethylacetal	3:1280	$\alpha,\alpha,\beta$ -Trichloro- <i>n</i> -butyric acid
3:1270	Trichloroacetaldehyde hydrate	3:1831	$\alpha,\alpha,\gamma$ -Trichloro- <i>n</i> -butyric acid
3:1150	Trichloroacetic acid	3:0925	$\alpha,\beta,\beta$ -Trichloro- <i>n</i> -butyric acid
3:6575	Trichloroacetic acid anhydride	3:1000	$\gamma,\gamma,\gamma$ -Trichloro- <i>n</i> -butyric acid
3:5620	$\alpha,\alpha,\alpha$ -Trichloroacetone	3:3448	3,4,5-Trichlorocatechol
3:5957	$\alpha,\alpha,\gamma$ -Trichloroacetone	3:5230	1,2,3-Trichloro-2-(chloromethyl)-butane
3:6874	$\omega,\omega,\omega$ -Trichloroacetophenone	3:9084	1,1,3-Trichloro-2-(chloromethyl)-propane
3:5420	Trichloroacetyl chloride	3:6335	1,2,3-Trichloro-2-(chloromethyl)-propane
3:1840	$\alpha,\beta,\beta$ -Trichloroacrylic acid	3:1820	1,1,1-Trichloro-2-( <i>o</i> -chlorophenyl)-2-( <i>p</i> -chlorophenyl)-ethane
3:5845	Trichloroacryloyl chloride	3:9867	1,1,1-Trichloro-2-( <i>m</i> -chlorophenyl)-2-( <i>p</i> -chlorophenyl)-ethane
3:2212	2,3,4-Trichlorobenzal (di)-chloride	3:9865	1,1,1-Trichloro-2,2-bis-( <i>o</i> -chlorophenyl)ethane
3:2178	2,3,6-Trichlorobenzal (di)-chloride	3:3298	1,1,1-Trichloro-2,2-bis-( <i>p</i> -chlorophenyl)ethane
3:6910	2,4,5-Trichlorobenzal (di)-chloride	3:0618	2,4,6-Trichloro- <i>m</i> -cresol
3:0142	2,4,6-Trichlorobenzal (di)-chloride	3:1280	" Trichlorocrotonic acid "
3:2445	2,3,4-Trichlorobenzaldehyde	3:4742	4,5,6-Trichloro-2,3-dimethyl-phenol
3:1060	2,3,5-Trichlorobenzaldehyde	3:4707	3,5,6-Trichloro-2,4-dimethyl-phenol
3:2257	2,3,6-Trichlorobenzaldehyde	3:4709	3,4,6-Trichloro-2,5-dimethyl-phenol
3:3375	2,4,5-Trichlorobenzaldehyde	3:4747	2,5,6-Trichloro-3,4-dimethyl-phenol
3:1200	2,4,6-Trichlorobenzaldehyde	3:4713	2,4,6-Trichloro-3,5-dimethyl-phenol
3:2440	3,4,5-Trichlorobenzaldehyde	3:1420	1,1,1-Trichloro-2,2-diphenyl-ethane
3:0930	1,2,3-Trichlorobenzene	3:5760	3,3,3-Trichloro-1,2-epoxypropane
3:6420	1,2,4-Trichlorobenzene	3:5085	1,1,1-Trichloroethane
3:1400	1,3,5-Trichlorobenzene	3:5330	1,1,2-Trichloroethane
3:1400	<i>sym.</i> -Trichlorobenzene	3:5330	<i>unsym.</i> -Trichloroethane
3:6120	<i>unsym.</i> -Trichlorobenzene	3:5775	2,2,2-Trichloroethanol-1
3:0990	<i>vic.</i> -Trichlorobenzene	3:5775	$\beta,\beta,\beta$ -Trichloroethyl alcohol
3:4810	2,3,4-Trichlorobenzoic acid	3:5170	1,1,2-Trichloroethylene
3:4485	2,3,5-Trichlorobenzoic acid	3:9308	3,3,6-Trichlorohexadiene-1,4
3:4500	2,3,6-Trichlorobenzoic acid	3:9302	3,4,6-Trichlorohexatriene-1,2,4
3:4630	2,4,5-Trichlorobenzoic acid	3:9326	1,1,2-Trichlorohexene-1
3:4545	2,4,6-Trichlorobenzoic acid	3:5840	" Trichlorohydrin "
3:4920	3,4,5-Trichlorobenzoic acid	3:4052	2,3,6-Trichlorohydroquinone
3:4672	2,3,5-Trichlorobenzoquinone-1,4	3:3520	2,4,6-Trichloro-3-hydroxybenzaldehyde
3:2212	2,3,4-Trichlorobenzylidene (di)-chloride	3:4444	3,5,6-Trichloro-2-hydroxyhydroquinone
3:2178	2,3,6-Trichlorobenzylidene (di)-chloride	3:0846	$\beta,\beta,\beta$ -Trichloroisopropyl alcohol
3:6910	2,4,5-Trichlorobenzylidene (di)-chloride	3:5785	$\beta,\beta,\beta$ -Trichloroisopropyl chloride
3:0142	2,4,6-Trichlorobenzylidene (di)-chloride	3:5050	Trichloromethane
3:0052	1,2,3-Trichlorobutadiene-1,3	3:6100	1,2,3-Trichloro-2-methylbutane
3:9086	1,1,3-Trichlorobutane	3:4755	2,3,3-Trichloro-2-methylbutane
3:5935	1,2,3-Trichlorobutane	3:9216	4,4,4-Trichloro-2-methylbutane
3:5680	2,2,3-Trichlorobutane	3:1915	<i>bis</i> -(Trichloromethyl) carbonate
3:1336	2,2,3-Trichlorobutanol-1	3:5515	Trichloromethyl chlorocarbonate
3:5955	1,1,1-Trichlorobutanol-2	3:5515	Trichloromethyl chloroformate
3:9064	2,3,4-Trichlorobutene-1		
3:9062	1,2,4-Trichlorobutene-2		
3:9062	1,3,4-Trichlorobutene-2		
3:9064	1,2,3-Trichlorobutene-3		
3:6180	$\beta,\beta,\beta$ -Trichloro- <i>ter</i> -butyl acetate		
3:2662	$\beta,\beta,\beta$ -Trichloro- <i>ter</i> -butyl alcohol		
3:5910	$\alpha,\alpha,\beta$ -Trichloro- <i>n</i> -butyraldehyde		

3:3510	2,5- <i>bis</i> -(Trichloromethyl)-1,3-dioxolanone-4	3:0425	2,3,4-Trichlorotoluene
3:0618	2,4,6-Trichloro-3-methylphenol	3:0610	2,3,5-Trichlorotoluene
3:5710	1,1,2-Trichloro-2-methylpropane	3:0625	2,3,6-Trichlorotoluene
3:5885	1,2,3-Trichloro-2-methylpropane	3:2100	2,4,5-Trichlorotoluene
3:2662	1,1,1-Trichloro-2-methylpropanol-2	3:0380	2,4,6-Trichlorotoluene
3:5025	1,1,3-Trichloro-2-methylpropene-1	3:0580	3,4,5-Trichlorotoluene
3:5605	3,3,3-Trichloro-2-methylpropene-1	3:4742	Trichloro- <i>o</i> -3-xylene
3:5605	1,1,1-Trichloro-2-methylpropene-2	3:4747	Trichloro- <i>o</i> -4-xylene
3:0290	Trichloromethyl trichloroacetate	3:4707	Trichloro- <i>m</i> -4-xylene
3:2125	1,2,3-Trichloronaphthalene	3:4713	Trichloro- <i>m</i> -5-xylene
3:2490	1,2,4-Trichloronaphthalene	3:4709	Trichloro- <i>p</i> -xylene
3:1930	1,2,5-Trichloronaphthalene	3:0860	Tridecanoyl chloride
3:2515	1,2,6-Trichloronaphthalene	3:0859	<i>n</i> -Tridecyl chloride
3:2325	1,2,7-Trichloronaphthalene	3:8055	Triethylcarbonyl chloride
3:2220	1,2,8-Trichloronaphthalene	3:9588	Triethylene glycol mono(chloroacetate)
3:3015	1,3,5-Trichloronaphthalene	3:6655	" Triglycol dichloride "
3:1975	1,3,6-Trichloronaphthalene	3:7450	Trimethylacetyl chloride
3:3400	1,3,7-Trichloronaphthalene	3:0338	$\alpha,\beta,\gamma$ -Trimethylallyl chloride
3:2420	1,3,8-Trichloronaphthalene	3:7520	$\beta,\gamma,\gamma$ -Trimethylallyl chloride
3:4005	1,4,5-Trichloronaphthalene	3:0750	2,4,6-Trimethylbenzoyl chloride
3:1635	1,4,6-Trichloronaphthalene	3:0701	2,3,6-Trimethylbenzyl chloride
3:3300	2,3,5-Trichloronaphthalene	3:0702	2,4,5-Trimethylbenzyl chloride
3:2453	2,3,6-Trichloronaphthalene	3:0372	2,4,6-Trimethylbenzyl chloride
3:2300	Trichloroparaldehyde	3:8145	$\alpha,\alpha,\beta$ -Trimethyl- <i>n</i> -butyryl chloride
3:2185	2,3,4-Trichlorophenol	3:7045	Trimethylcarbonyl chloride
3:1340	2,3,5-Trichlorophenol	3:7165	Trimethylcarbonyl hypochlorite
3:1160	2,3,6-Trichlorophenol	3:0418	Trimethylchloryl chloride
3:1620	2,4,5-Trichlorophenol	3:5450	Trimethylene (di)chloride
3:1673	2,4,6-Trichlorophenol	3:8285	Trimethylene chlorohydrin
3:2885	3,4,5-Trichlorophenol	3:8310	Trimethylene chlorohydrin acetate
3:4335	2,4,5-Trichlorophenoxyacetic acid	3:8030	Trimethylethylene chlorohydrin
3:4030	2,4,6-Trichlorophloroglucinol	3:7975	Trimethylethylene dichloride
3:9033	2,2,3-Trichloropropanol-1	3:9324	Trimethylpropargyl chloride
3:5270	1,1,1-Trichloropropane	3:7335	Trimethylvinyl chloride
3:5630	1,1,2-Trichloropropane	3:3410	Triphenylchloromethane
3:5660	1,1,3-Trichloropropane	3:3410	Triphenylmethyl chloride
3:5475	1,2,2-Trichloropropane	3:1915	Triphosgene
3:5840	1,2,3-Trichloropropane	3:9742	Tri- <i>n</i> -propylcarbonyl chloride
3:0846	1,1,1-Trichloropropanol-2	3:3410	Triyl chloride
3:5620	1,1,1-Trichloropropanone-2		
3:5957	1,1,3-Trichloropropanone-2		
3:5395	1,1,2-Trichloropropene-1	3:0800	<i>n</i> -Undecanoyl chloride
3:5650	1,2,3-Trichloropropene-1	3:8903	<i>n</i> -Undecyl chloride
3:5345	3,3,3-Trichloropropene-1		
3:5345	1,1,1-Trichloropropene-2		
3:9033	$\alpha,\alpha,\beta$ -Trichloropropionaldehyde		
3:1275	$\alpha,\alpha,\beta$ -Trichloropropionic acid		
3:5760	$\omega,\omega,\omega$ -Trichloropropylene oxide	3:7740	<i>n</i> -Valeryl chloride
3:3448	3,4,5-Trichloropyrocatechol	3:7010	Vinyl chloride
3:4782	4,5,6-Trichloropyrogallol	3:5005	Vinylidene (di)chloride
3:4672	Trichloroquinone		
3:2174	2,4,6-Trichlororesorcinol		
3:6540	$\omega,\omega,\omega$ -Trichlorotoluene	3:8710	<i>o</i> -Xylyl chloride
		3:8700	<i>m</i> -Xylyl chloride
		3:8660	<i>p</i> -Xylyl chloride
		3:1040	<i>o</i> -Xylylene (di)chloride
		3:0310	<i>m</i> -Xylylene (di)chloride
		3:2525	<i>p</i> -Xylylene (di)chloride



## 3:4170 3-CHLORONAPHTHOL-1

 $C_{10}H_7OCl$ 

Beil. VI —

VI<sub>1</sub>—VI<sub>2</sub>-(581)

M.P. 143° (1)

134-135° (2)

Ndls. from lgr. (2),  $C_6H_6$ , alc. or 80% AcOH (1). — Volatile with steam (1).

[For prepn. of  $\bar{C}$  from 3-chloronaphthylamine-1 (1) via diazotization and hydrolysis of the diazonium salt with steam see (1); from 2,3,4-trichloronaphthol-1 [Beil. VI-612] by partial reduction with H1 ( $D = 1.7$ ) in AcOH on oilg. 7 hrs. (100% yield) see (2)]

 $\bar{C}$  is sol in aq alk., and the result. soln. couples with solns. of diazonium salts (1).

$\bar{C}$  with  $Br_2$  aq. (and alk.?) gives 3-chloro-2,4-dibromonaphthol-1, pr. from 90% formic acid, m.p. 112° (1).

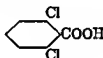
[ $\bar{C}$  in 10% aq KOH shaken with  $Me_2SO_4$  for 20 min. gives (81% yield (2)) 3-chloronaphthol-1 methyl ether, oil, b.p. 162-164° at 18 mm. (2).]

③ 3-Chloro-1-naphthyl acetate: ndls. from lgr., m.p. 69° (2). [From  $\bar{C}$  with acetyl chloride in  $C_6H_6$  on refluxing 3 hrs. in  $C_6H_6$  (66% yield (2)).]

④ 3-Chloro-1-naphthyl benzoate: ndls. from lgr., m.p. 118-119° (2). [From  $\bar{C}$  in 10% aq. KOH on shaking with  $BzCl$  (71% yield (2)).]

3:4170 (1) Hodgson, Elliott, *J. Chem. Soc.* 1934, 1707. (2) Franzen, Stäuble, *J. prakt. Chem.* (2) 103, 385-387 (1922).

## 3:4200 2,6-DICHLORO BENZOIC ACID

 $C_7H_4O_2Cl_2$ 

Beil. IX - 343

IX<sub>1</sub>-(141)

M.P. 144° (1) (2)

143.7° (3)

143-144° (4)

141.5-142.5° (5)

Many recorded m.p.'s lower than these values [cf. Beil. IX-343 and (3)] were on sample now known to have been impure.

Cryst. from lgr. (1) or mixt. of  $C_6H_6$  + lgr. (4) (3); pr. from aq., thls. from  $C_6H_6$ , ndl from alc. — Can also be purified by distn. in vac. (1). — Volatile with steam (?).

[For prepn. of  $\bar{C}$  from 2,6-dichlorotoluene (3:6270) (57% yield (4)) via brominat to 2,6-dichlorobenzyl bromide, conversion to corresp. acetate, and oxidn. of latter v  $KMnO_4$  see (1) (4); from 2,6-dichlorobenzaldehyde by oxidn. with  $KMnO_4$  see (2); older less satisfactory methods see Beil. IX-343.]

$\bar{C}$  on htg. begins to lose  $CO_2$  at 235° (5). [ $\bar{C}$  htd. with a large excess 50% aq. KOH 150° for 24 hrs. was recovered unchanged to extent of 90% (9).]

$\bar{C}$  on nitration under stated conditions (1) gives 94% yield 2,6-dichloro-3-nitrobenzoic acid, cryst. from toluene, m p. 152° (1).

$\bar{C}$  (as  $K\bar{A}$ ) htd. with aniline +  $K_2CO_3$  + Cu in amyl alc. gives small yield of diphenyl aminocarboxylic acid-2, cryst. from  $C_6H_6$ , m.p. 181° (1). [Note loss of both chlorine atoms.]

$\bar{C}$  htd. with acetamide for 6 hrs. at 225-235° gave 93% yield (5) *m*-dichlorobenzen (3:5960), b.p. 172°.

$\bar{C}$  htd. with  $PCl_5$  (6) or with  $SOCl_2$  + pyridine (4) yields 2,6-dichlorobenzoyl chloride, h.p. 142-143° at 21 mm. (6), 126-128° at 18 mm. (7).

3:1055 2-CHLORO-3-METHYLPHENOL  
(2-Chloro-*m*-cresol)

C<sub>7</sub>H<sub>7</sub>OCl

Beil. VI —

VI<sub>1</sub>—VI<sub>2</sub>-(353)

M.P. 55-56° (1) B.P. abt. 194° (1)  
49-50° (2)

Transparent cryst. (1) (2) from pet. eth. — Very spar sol cold aq.; pronounced phenolic odor (1).

[For prepn. from *m*-cresoldisulfonic acid by chlorination see (2); from 2-nitro-3-methylphenol via 2-amino-3-methylphenol see (2), from 2-chloro-3-methylanisole by boilg. with HI see (1).]

$\bar{C}$  treated with (CH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub> + aq NaOH gives its methyl ether, 2-chloro-3-methylanisole, pr. from light pet. eth., m.p. 24.2°, b.p. 218.5° (1) [This methyl ether on oxidn. with dil. KMnO<sub>4</sub> (7¼ hrs. for 5 g.) gave (1) 2-chloro-3-methoxybenzoic acid, stout colorless rectangles, m.p. 160.5° (1), 160° (3), Neut. Eq. 186.5.]

② 2-Chloro-3-methylphenyl benzoate: from  $\bar{C}$  + BzCl + pyridine, pr. from alc., m.p. 55-56° (2). [Note that this value is numerically the same as  $\bar{C}$  and that the deriv. must be distinguished from orig.  $\bar{C}$ , e.g., by mixed m.p. or behavior with alk.]

③ 2-Chloro-3-methylphenyl benzenesulfonate: from  $\bar{C}$  + benzenesulfonyl chloride + pyridine; pl. from alc., m.p. 58-58.5° (2) [See note for above deriv.]

④ 2-Chloro-3-methylphenyl *p*-toluenesulfonate: from  $\bar{C}$  + *p*-toluenesulfonyl chloride + pyridine; pr. from alc. m.p. 90° (2) [Note that this deriv. does not distinguish  $\bar{C}$  from 6-chloro-3-methylphenol (3:0700) or 4-chloro-3-methylphenol (3:1535).]

3:1053 (1) Gibson, J. Chem. Soc. 1926, 1424-1428 (2) Huston, Chem. J. Am. Chem. Soc. 55, 4214-4218 (1933). (3) Hodgson, Beard, J. Chem. Soc. 1926, 150

3:1057 4,4'-DICHLORODIPHENYL-  
METHANE  
(Di-(*p*-chlorophenyl)methane)

C<sub>12</sub>H<sub>10</sub>Cl<sub>2</sub>

Beil. V - 509

V<sub>1</sub>—V<sub>2</sub>-(501)

M.P. 55-56° (1) B.P. 337° at 760.5 mm. (5)  
55° (2) (3) (4) (5) 186-190° at 18 mm. (1)  
54-55° (7) 208-219° at 15 mm. (3)

Colorless ndls. from MeOH.

[For prepn. of  $\bar{C}$  from 4,4'-dichlorobenzophenone (3:1270) by reduction with conc. HI + red P in boilg. AcOH (4) or as by-prod. of reduction with Zn dust + AcOH + dil. H<sub>2</sub>SO<sub>4</sub> (5) see indic. refs.; from 4,4'-diaminodiphenylmethane [Beil. XII-238, XII<sub>1</sub>-(71)] by tetrazotization and subsequent use of Cu<sub>2</sub>Cl<sub>2</sub> reaction (59% yield) see (1).]

[For prepn. of  $\bar{C}$  from chlorobenzene (3:7903) by action of *sym*-dichloro-dimethyl ether (3:5245) in pres. of ZnCl<sub>2</sub> (3) or better (alm. 100% yield (3)) conc. H<sub>2</sub>SO<sub>4</sub> at 40°, or by action in pres. of H<sub>2</sub>SO<sub>4</sub> of various other formaldehyde derivs. (6), see indic. refs.; from *p*-chlorobenzyl chloride (3:0220) with chlorobenzene (3:7903) + conc. H<sub>2</sub>SO<sub>4</sub> (67% yield (3)) see indic. refs.]

[For prepn. of  $\bar{C}$  from "DDT" (3:3298), from 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethylene (3:2138), or from di-(*p*-chlorophenyl)acetic acid (3:4612) by action of KOH in ethylene glycol refluxed 8-10 hrs. (alm. 100% yield) see (2).]

[For formn. of  $\bar{C}$  (21% yield) from hydrazone of 4,4'-dichlorobenzophenone (3:4270) via Wolff-Kishner reduction see (7).]

$\bar{C}$  on oxidn. with  $\text{CrO}_3/\text{AcOH}$  readily gives (3) 4,4'-dichlorobenzophenone (3:4270), m.p. 145° (3).

$\bar{C}$  on nitration by addn. to 8 pts. fuming  $\text{HNO}_3$  ( $D = 1.5$ ) with water cooling gives (1) 3,3'-dinitro-4,4'-dichlorophenylmethane, white pl. from  $\text{AcOH}$ , m.p. 198-199° (1), 196° (3); this prod. with piperidine splits out 2 moles  $\text{HCl}$  giving (1) 3,3'-dinitro-4,4'-dipiperidinodiphenylmethane, m.p. 183-184° (1). — [Note, however, that  $\bar{C}$  dislvd. in 9-10 wt. pts. conc.  $\text{HNO}_3$  ( $D = 1.42$ ) and kept at 100° for 1 hr. (3) gives some of the above dinitro derivative but is also in part oxidized and nitrated (or vice versa) with formn. of 3,3'-dinitro-4,4'-dichlorobenzophenone, ndls. from alc., m.p. 132° (3); see also text of 4,4'-dichlorobenzophenone regarding nitration.]

3:1057 (1) LeFevre, Turner, *J. Chem. Soc.* 1927, 1120. (2) White, Sweeney, *U.S. Pub. Health Repts.* 60, 66-71 (1915). (3) Stephen, Short, Gladding, *J. Chem. Soc.* 117, 522-523 (1920).

(4) "

(6)

405f

3:1058  $\beta,\beta$ -DICHLOROPROPIONIC ACID  $\text{C}_3\text{H}_4\text{O}_2\text{Cl}_2$  Beil. II -252  
 $\text{Cl}_2\text{CH}.\text{CH}_2.\text{COOH}$  II—  
 II—

M.P. 56° (1)

Colorless cryst., eas. sol. aq., alc., ether,  $\text{C}_6\text{H}_6$ , or  $\text{CHCl}_3$ .

[For prepn. of  $\bar{C}$  from  $\beta$ -chloroacrylic acid (3:2240) by addn. of 1  $\text{HCl}$  with 40% aq.  $\text{HCl}$  in s.t. at 80-85° for 35-40 hrs. (yield not stated) see (1).]

$\bar{C}$  with alc.  $\text{KOH}$  splits out 1  $\text{HCl}$  giving (1)  $\beta$ -chloroacrylic acid (3:2240).

$\bar{C}$  with  $\text{SOCl}_2$  at 75-80° for 3-4 hrs. gives (2)  $\beta,\beta$ -dichloropropionyl chloride (3:9032-A).

— Methyl  $\beta,\beta$ -dichloropropionate: unreported.

— Ethyl  $\beta,\beta$ -dichloropropionate: b.p. 171-175° (1). [From  $\bar{C}$  in  $\text{EtOH}$  with dry  $\text{HCl}$  (1).]

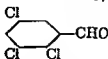
①  $\beta,\beta$ -Dichloropropionamide: ndls. from  $\text{CHCl}_3$ , m.p. 140° (1). [From ethyl  $\beta,\beta$ -dichloropropionate (above) with conc. aq.  $\text{NH}_4\text{OH}$  on shaking at room temp. (1).]

—  $\beta,\beta$ -Dichloropropionanilide: unreported.

—  $\beta,\beta$ -Dichloropropion-*p*-toluidide: unreported.

3:1058 (1) Otto, *Ann.* 239, 266-272 (1887). (2) Leimu, *Ber.* 70, 1050 (1937).

3:1060 2,3,5-TRICHLOROBENZALDEHYDE  $\text{C}_7\text{H}_3\text{OCl}_3$  Beil. S.N. 635



M.P. 56° (1)

Colorless ndls. (from dil. alc.) with characteristic pungent odor. — Volatile with steam.

— [Note that a patent abstract gives m.p. as 75-76° (2).]

[For prepn. of  $\bar{C}$  from 3-amino-2,5-dichlorobenzaldehyde (presumably by diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reaction) see (1).]

$\bar{C}$  on oxidn. with neutral  $\text{KMnO}_4$  gives (1) 2,3,5-trichlorobenzoic acid (3:4485), m.p. 162-163°.

$\bar{C}$  with  $PCl_5$  should give 2,3,5-trichlorobenzal (di)chloride, but this compd. is unreported in the literature.

- 2,3,5-Trichlorobenzaldoxime: unreported.
- 2,3,5-Trichlorobenzaldehyde phenylhydrazone: unreported.
- 2,3,5-Trichlorobenzaldehyde *p*-nitrophenylhydrazone: unreported.
- 2,3,5-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

3:1060 (1) Hodgson, Beard, *J. Chem. Soc.* 1927, 2381-2382. (2) Chem. Fabrik Griesheim-Elektron, Brit. 251,511, May 27, 1926; *Cent.* 1926, II 2355; [*C.A.* 21, 1361 (1927)], French 603,650, April 20, 1926; *Cent.* 1926, II 2355; not in *C.A.*

3:1085 DICHLOROACETALDEHYDE  
HYDRATE


 $\text{C}_2\text{H}_4\text{O}_2\text{Cl}_2$ 

Beil. I - 614

 $\text{I}_1 -$   
 $\text{I}_2 -$ 

M.P. 56-57° (1) (4)      B.P. 118-121° (1)  
55-56° (2)              96-97.5° (2)

Cryst. from  $\text{C}_6\text{H}_6$  (3). — Eas. sol. aq. or ether; sol.  $\text{CS}_2$ .

[For prepn. of  $\bar{C}$  from dichloroacetaldehyde (3:5180) with a limited amt. of cold aq. see (2); for formn. of  $\bar{C}$  from  $\alpha,\beta,\beta$ -trichloroethyl ethyl ether with aq. see (2); for formn. of  $\bar{C}$  as by-product of actn. of  $\text{Cl}_2$  on paraldehyde in prepn. of butyrylchloral (3:5910) see (2); for formn. of  $\bar{C}$  from chloral hydrate with  $\text{Al/Hg} + \text{aq.}$  see (5).]

$\bar{C}$  with conc.  $\text{H}_2\text{SO}_4$  yields (3) dichloroacetaldehyde (3:5180), b.p. 89°.

3:1085 (1) Denaro, *Gazz. chim. ital.* 14, 119-120 (1884). (2) Oddo, Mameli, *Gazz. chim. ital.* 33, II 398-399 (1903). (3) Friedrich, *Ann.* 206, 251-254 (1880). (4) Ingold, *J. Chem. Soc.* 125, 1537 (1924). (5) Deodhar, *J. Indian Chem. Soc.* 11, 84 (1934).

3:1100 2-CHLOROBENZOQUINONE-1,4  
(Chloroquinone)


 $\text{C}_6\text{H}_3\text{O}_2\text{Cl}$ 

 Beil. VII - 630  
VII<sub>1</sub>-(346)

M.P. 57°              (1) (2) (3) (4) (5) (6) (7) (14) (15)  
56.0-56.5° cor. (8)  
56°                  (9)  
55-57°              (10)  
54°                  (11)

[See also 2-chlorohydroquinone (3:3130).]

Pale yel. cryst.; eas. sol. aq., alc., ether,  $\text{CHCl}_3$ . — Volatile even at ord. tem. — Gradually dec. by light (3) (for study of photochem. decompn. in alc. see (12)). — Sol. in conc.  $\text{H}_2\text{SO}_4$  on warming with brown black color.

[For prepn. of  $\bar{C}$  from 2-chlorohydroquinone (3:3130) by oxidn. with  $\text{NaClO}_3 + \text{H}_2\text{SO}_4 + \text{V}_2\text{O}_5$  in  $\text{AcOH}$  (92% yield (13)), with  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$  (yield: 89% (14), 84% (1)) (7), with  $\text{MnO}_2 + \text{dil. H}_2\text{SO}_4$  (56% yield (1)), or with  $\text{PbO}_2$  in  $\text{C}_6\text{H}_6$  (2) see indic. refs.; from 2-chloro-4-aminophenol [Beil. XIII-510, XIII<sub>1</sub>-(181)] by oxidn. with  $\text{K}_2\text{Cr}_2\text{O}_7 +$

$\text{H}_2\text{SO}_4$  (68% yield (8)) (10) (15) see indie. refs.; from benzoquinone-1,4 (1:9025) in  $\text{OCl}_2$  with  $\frac{1}{2}$  mole  $\text{HCl}$  gas see (9); for formn. of  $\bar{\text{C}}$  (together with other prods.) from oxidn. of copper salt of quinic acid [Beil. X-535, X<sub>1</sub>-270] with  $\text{MnO}_2$ ,  $\text{NaCl}$  + dil.  $\text{H}_2\text{SO}_4$  see (16)]

[For use of  $\bar{\text{C}}$  as vulcanization accelerator see (17); for use as seed disinfectant see (18); for study of bactericidal action see (19).]

$\bar{\text{C}}$  on reductn. with aq.  $\text{SO}_2$  gives (16) (7) 2-chlorohydroquinone (3:3130) (note, however, that  $\bar{\text{C}}$  in dil. aq.  $\text{NaOH}$  under  $\text{N}_2$  with  $\text{SO}_2$  is in part reduced to 2-chlorohydroquinone and in part sulfonated (20)). [For studies on oxidn.-reductn. potential of system  $\bar{\text{C}}$  + 2-chlorohydroquinone (3:3130) see (1) (2) (3) (21) (22) (23) (24).] — [ $\bar{\text{C}}$  with 2-chlorohydroquinone (3:3130) yields (1) (16) (25) the corresp. quinhydrone, monohydrate, violet pr. with green shimmer, m.p. 70–72° (25), anhydrous form, m.p. 93–94° (25), 67° (1);  $\bar{\text{C}}$  with hydroquinone (1:1590) gives (25) (6) corresp. quinhydrone, dark green ndls. from alc., m.p. 132–133° (25), 130–135° (6).]

[ $\bar{\text{C}}$  in  $\text{CHCl}_3$  with  $\text{HCl}$  gas (7) (26) or  $\bar{\text{C}}$  with hot conc.  $\text{HCl}$  (83% yield (10)) gives only 2,5-dichlorohydroquinone (3:4690), but  $\bar{\text{C}}$  in ether with  $\text{HCl}$  gas (26) or  $\bar{\text{C}}$  dislvd. in cold dil.  $\text{HCl}$  ( $D = 1.10$ ) (26) gives both 2,3-dichlorohydroquinone (3:4220) and 2,5-dichlorohydroquinone (3:4690);  $\bar{\text{C}}$  refluxed with conc.  $\text{HBr}$  gives (27) 2-chloro-5-bromohydroquinone [Beil. VI-853], ndls. m.p. 171–172° (28) (diacetate, m.p. 145–146° (28));  $\bar{\text{C}}$  in alc. with  $\text{KCN}$  +  $\text{H}_2\text{SO}_4$  gives in good yield (29) 3,6-dihydroxyphthalonitrile (2,3-dicyanohydroquinone) [Beil. X-551]]

[ $\bar{\text{C}}$  with  $\text{Ac}_2\text{O}$  + trace  $\text{H}_2\text{SO}_4$  yields (29) a chloro-hydroxyhydroquinone triacetate, ndls. from alc., m.p. 96–97° (29);  $\bar{\text{C}}$  with  $\text{AcCl}$  gives (28) 2,5-dichlorohydroquinone diacetate, m.p. 141°;  $\bar{\text{C}}$  with  $\text{AcBr}$  gives (28) 2-chloro-5-bromohydroquinone diacetate, m.p. 145–146° (28)]

[ $\bar{\text{C}}$  with 2,3-dimethylbutadiene-1,3 (1:8050) gives an adduct which upon oxidn. yields (30) 2-chloro-6,7-dimethylnaphthoquinone-1,4; for reactn. of  $\bar{\text{C}}$  with diazotized aniline see (31); for addn. prods. of  $\bar{\text{C}}$  with hexamethylbenzene (1:7205) see (5).]

[ $\bar{\text{C}}$  in alc. or  $\text{AcOH}$  on warming with aniline gives (32) 2,5-dianilinoenzoquinone-1,4 [Beil. XIV-138, XIII<sub>1</sub>-(413)], red-hr. scales, m.p. 345° u.c.]

[ $\bar{\text{C}}$  in dil. alc. with  $\text{NH}_4\text{OH.HCl}$  as directed (33) gives 2-chlorobenzoquinone-1,4-monoxime-4 (purified (with difficulty) by conv. to the mixt. of stereoisomeric oxime acetates followed by hydrolysis), m.p. 142° (34), 148° dec. (35); this prod. by special treatment yields n dioxime [Beil. VII-632].]

$\bar{\text{C}}$  in cold dil. alc. with semicarbazide  $\text{HCl}$  gives (36) 2-chlorobenzoquinone-1,4-semicarbazone-4, deep yel. cryst. from acetone + pet. ether, m.p. 185° dec. (36); this prod. on hoilg. with dil. aq.  $\text{NaOH}$  yields o-chlorophenol (3:5980) +  $\text{N}_2$  +  $\text{CO}_2$  +  $\text{NH}_3$  (36);  $\bar{\text{C}}$  does not give n bis-semicarbazone (36).

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3:1115  $\beta$ -CHLOROETHYL PHENYL  
KETONE ClC1=CC=CC=C1C(=O)CCCl  $C_9H_9OCl$  Beil. VII - 302  
( $\beta$ -Chloropropiophenone) VII<sub>1</sub>-(161)

M.P. 57-58° (1)  
57° (2)  
55-50° (3)  
49-50° (4) (5)  
49° (3)

See text.

Lfts. from pet. ether (5), alc. (1) (5), or ether (2), eas. sol. in org. solv. except lgr. —  
C̄ on distn. even under reduced press. loses HCl with partial conversion (2) to phenyl  
vinyl ketone; nevertheless in small amts. of less than 10 g C̄ may be distd below 2 mm (3);  
in general, however, unnecessary htg of C̄ should be avoided (4).

[For prepn. of C̄ from  $\beta$ -chloropropionyl chloride (3 5690) with  $C_6H_6$  +  $AlCl_3$  (yield:  
90% (1), 80-90% (6), 65% (5)) see indie. refs. (note, however, that this method is best  
suited for small runs (6) since with large units much  $\omega$ -benzylacetophenone [Beil. VII-444,  
VII<sub>1</sub>-(237)], m p. 72°, is also formed (6) (4); furthermore that C̄ prepd by this method  
melts at 49° even when white, unless it is treated with decolorizing carbon (3), for prepn.  
from benzoyl chloride (3:6240) + ethylene +  $AlCl_3$  (87-92% yield) in special apparatus  
see (3); for prepn. of C̄ from phenyl vinyl ketone + HCl gas in dry ether see (2); for formn.  
of C̄ from ethyl phenyl ketone (propiophenone) (1-5525) +  $Cl_2$  see (7) ]

[C̄ htd 15-30 min. in AcOH with  $1\frac{1}{2}$  moles NaOAc or KOAc, then poured into aq. and  
neutralized with  $K_2CO_3$ , gives (8)  $\beta$ -acetoxypropiophenone, lfts from MeOH, m.p. 53-54°  
(8); C̄ in hot alc. treated with KOAc, then with aq. NaCN, gives (65% yield (9))  $\beta$ -cyano-  
propiophenone, lfts. from alc., m.p. 76° (2,4-dinitrophenylhydrazone, m p. 141°; corresp.  
 $\beta$ -benzoylpropionic acid, m.p. 116° (9)) ]

[C̄ under certain circumstances reacts as potential phenyl vinyl ketone: e.g., C̄ + KOAc  
in hot MeOH treated with phenyl-nitromethane + NaOMe gives (82% yield (10)) (pro-  
sumably ]

$C_6H_6$  + p  
with desox  
1,5, m.p. 95° (monoxime, m.p. 131°; dioxime, m.p. 162°; 2,4-dinitrophenylhydrazone,  
m.p. 221°) (6) ]

C̄ in AcOH reduced with  $H_2$  + Adams cat gives (11) 3-chloro-1-phenylpropanol-1,  
b.p. 130-132° at 8 mm. (p-nitrobenzoate, m.p. 62-63°) (11).

[For study of rate of reactn. of C̄ with KI in acetone see (5), for study of C̄ with Na +  
liq  $NH_3$  see (12); for behavior of C̄ with anthrone see (13) (14) (15); for reactn of C̄ with  
 $C_6H_5MgBr$  yielding  $\omega$ -benzylacetophenone ( $\beta$ -phenylpropiophenone) (cf. above) see



$\bar{C}$  dislvd. in alc. warmed at 60° with  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  dislvd. in aq. gives (5) (73% yield (6)) bis-(*p*-methylphenacyl)sulfide, pale yel. ndls. from alc., m.p. 88° (5); 88.8–89.3° (6). [For detn. of  $\bar{C}$  by titration of residual chloride ion from this reaction see (5).]

[For reactions of  $\bar{C}$  with phenol + KOH + Cu see (7); with phenyl-*p*-bromophenyl-, *p*-nitrophenyl-, *o*-tolyl-, and *p*-tolyl-hydrazines see (5); with  $\text{Br}_2$  see (8); with KCN or KSCN see (9); with alc. NaOEt see (10).]

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### 3:1145 2,5-DICHLOROBENZALDEHYDE

$\text{C}_7\text{H}_4\text{OCl}_2$

Beil. VII -237

VII—



M.P. 58° (1) B.P. 231–233° (1)  
57–58° (2) (4) 230–233° (2)  
57° (3)

Ndls. from alc. (4). — Very eas. sol. alc., ether,  $\text{CHCl}_3$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CS}_2$ , AcOH (4). — Eas. volatile with steam (4). — Sol. in conc.  $\text{H}_2\text{SO}_4$  with olive-yel. color; repptd. in cryst. form on dilution (4) (8).

[For prepn. of  $\bar{C}$  from benzaldehyde (1:0195) by chlorination in presence of  $\text{SbCl}_5$  +  $\text{I}_2$  see (5) (1) (9); from 2,5-dichlorotoluene (3:6245) by chlorination to 2,5-dichlorobenzal (di)chloride (3:0490) (m.p. 42°) and hydrolysis of the latter with  $\text{CaCO}_3$  +  $\text{H}_2\text{O}$  see (1); from 5-nitro-2-chlorobenzaldehyde via reduction to 5-amino-2-chlorobenzaldehyde followed by diazotization + use of CuCl see (6).]

$\bar{C}$  with satd. aq.  $\text{NaHSO}_3$  soln. yields a cpd.,  $\bar{C} \cdot \text{NaHSO}_3$  (5), ndls. fairly eas. sol. aq. but dissociating on warming into  $\bar{C}$  + aq. (5).

$\bar{C}$  on oxidn. with  $\text{KMnO}_4$  (2) (4) yields 2,5-dichlorobenzoic ac. (3:4340), m.p. 152° (2), 152–153° (4). —  $\bar{C}$  with 50% aq. KOH (5) (1) (6) undergoes Cannizzaro reactn. giving (90% yield (6)) 2,5-dichlorobenzyl alc., cryst. from  $\text{C}_6\text{H}_6$ , m.p. 80° (1) (6), and (84% yield (7)) 2,5-dichlorobenzoic ac. (3:4340), cryst. from aq., m.p. 155° (5) (7). —  $\bar{C}$  on reductn. with 4% Na/Hg in alc. yields (1) 2,5-dichlorobenzyl alc., m.p. 80° (1).

$\bar{C}$  with  $\text{PCl}_5$  (3) gives (78% yield (3)) 2,5-dichlorobenzal (di)chloride (3:0490), b.p. 118–120° at 14 mm, m.p. 42° (8), 43° (3).

$\bar{C}$  on mononitration as specified (5) gives (100% yield (9)) a mixt. of two isomers; by recrystallization from MeOH (9) or EtOH (5) this mixt. gives (62% yield (9)) 2,5-dichloro-6-nitrobenzaldehyde, lfts. or ndls., m.p. 137° (5); the other more soluble isomer is 2,5-dichloro-3-nitrobenzaldehyde (10), m.p. 66–67° (5). [The latter yields a phenylhydrazone, or. ndls., m.p. 171°, a *p*-nitrophenylhydrazone, deep or. ndls., m.p. 290–292° dec., and on oxidn. with alk.  $\text{KMnO}_4$  yields 2,5-dichloro-3-nitrobenzoic ac., colorless ndls. from AcOH, m.p. 220° (10).]

[For conversion of  $\bar{C}$  to 2,5-dichlorostyrene (12) (13) via reaction with  $\text{MeMgX}$  giving (83% yield (12)) 2,5-dichlorophenyl-methyl-carbinol and dehydration of latter with  $\text{H}_2\text{SO}_4$  (37% yield (12)) see indic. refs.]



BINARY SYSTEMS CONTG.  $\bar{C}$ *Azotropic Systems*

$\bar{C}$  with pentachloroethane (3:5880) forms a const.-boilg. mixt., b.p. 161.8° at 760 mm., contg. 3.5 wt. %  $\bar{C}$  (25);  $\bar{C}$  with *p*-dichlorobenzene (3:0980) forms a const.-boilg. mixt., b.p. 174.0° at 760 mm., contg. about 12 wt. %  $\bar{C}$  (26);  $\bar{C}$  with *o*-bromotoluene forms a const.-boilg. mixt., b.p. 180.0° at 760 mm., contg. about 18 wt. %  $\bar{C}$  (26).]

*Other Physical Data on Binary Systems Contg.  $\bar{C}$* 

$\bar{C}$  + aq. [ $\bar{C}$  is eas. sol. aq.; for study of hydration at  $-35^\circ$  see (70) cf. (34); for f.p./compn. data see (3); for data on  $D_{20}^{20}$  (31) and  $D_{25}^{25}$  (71) of aq. solns. see indic. refs.; for  $n_D^{18}$  (8),  $n_D^{20}$  (31) cf. (73) see indic. refs.]

$\bar{C}$  +  $H_2SO_4$ . [For f.p./compn. data and diagram (no compd. formed) see (10).]

$\bar{C}$  +  $H_3PO_3$ . [For f.p./compn. data and diagram (no compd. formed) see (12).]

$\bar{C}$  + AcOH (1:1010). [For f.p./compn. data (no cpd.) (74),  $D_4^{25}$  (2), viscosity (2), and conductivity (1) see indic. refs.]

$\bar{C}$  + chloroacetic acid (3:1370). [For f.p./compn. data (74), eutectic, m.p. 17.5°, contg. 51.5 mole %  $\bar{C}$  (75), see indic. refs.]

$\bar{C}$  + dichloroacetic acid (3:6208). [For f.p./compn. data (74), eutectic, m.p.  $-11.0^\circ$ , contg. 36 mole %  $\bar{C}$  (75), see indic. refs.]

$\bar{C}$  + miscellaneous cpds. of Order 1. [For f.p./compn. data on following systems see indic. refs.]

$\bar{C}$  with hydrocarbons:  $\bar{C}$  +  $C_6H_6$  (1:7400) (5);  $\bar{C}$  + camphene (76).

$\bar{C}$  with alcohols:  $\bar{C}$  + *EtOH* (1:6130) (14);  $\bar{C}$  + *ter-BuOH* (1:6140) (14);  $\bar{C}$  + *ethyl alc.* (1:5945) (14);  $\bar{C}$  + *d-borneol* (1:5990) (14);  $\bar{C}$  + *l-menthol* (1:5940) (14);  $\bar{C}$  + *pinacol* (1:5805) (14);  $\bar{C}$  + *meso-erythritol* (1:5825) (6);  $\bar{C}$  + *d-mannitol* (1:5830) (14).

$\bar{C}$  with phenols:  $\bar{C}$  + *phenol* (1:1420) (14) (11);  $\bar{C}$  + *o-cresol* (1:1400) (11);  $\bar{C}$  + *m-cresol* (1:1730) (11);  $\bar{C}$  + *p-cresol* (1:1410) (11);  $\bar{C}$  + *guaiacol* (1:1405) (14);  $\bar{C}$  + *thymol* (1:1430) (11);  $\bar{C}$  +  $\alpha$ -*naphthol* (1:1500) (11);  $\bar{C}$  +  $\beta$ -*naphthol* (1:1540) (11);  $\bar{C}$  + *hydroquinone* (1:1590) (14).

$\bar{C}$  with aldehydes:  $\bar{C}$  + *benzaldehyde* (1:0195) (7);  $\bar{C}$  + *salicylaldehyde* (1:0205) (7);  $\bar{C}$  + *m-hydroxybenzaldehyde* (1:0055) (7);  $\bar{C}$  + *p-hydroxybenzaldehyde* (1:0060) (7);  $\bar{C}$  + *p-anisaldehyde* (1:0240) (7);  $\bar{C}$  + *vanillin* (1:0050) (7);  $\bar{C}$  + *piperalonal* (1:0010) (7).

$\bar{C}$  with ketones:  $\bar{C}$  + *acetophenone* (1:5515) (7);  $\bar{C}$  + *benzophenone* (1:5150) (7);  $\bar{C}$  + *p-methoxybenzophenone* (1:5170) (7);  $\bar{C}$  + *benzil* (1:9015) (7);  $\bar{C}$  + *dibenzalacetone* (1:9024) (7);  $\bar{C}$  + *benzoquinone-1,4* (1:9025) (7).

$\bar{C}$  with acids:  $\bar{C}$  + *acetic acid* (1:1010) (74);  $\bar{C}$  + *benzoic acid* (1:0715) (74);  $\bar{C}$  + *o-toluic acid* (1:0690) (74);  $\bar{C}$  + *m-toluic acid* (1:0705) (74);  $\bar{C}$  + *p-toluic acid* (1:0795) (74);  $\bar{C}$  + *phenylacetic acid* (1:0665) (74);  $\bar{C}$  + *cinnamic acid* (1:0735) (74);  $\bar{C}$  + *crotonic acid* (1:0425) (74).

$\bar{C}$  with esters:  $\bar{C}$  + *EtOAc* (1:3015) (5);  $\bar{C}$  +  $\alpha$ -*naphthyl acetate* (1:2124) (5);  $\bar{C}$  +  $\beta$ -*naphthyl acetate* (1:2273) (5);  $\bar{C}$  + *methyl benzoate* (1:3586) (5);  $\bar{C}$  + *ethyl benzoate* (1:3721) (5);  $\bar{C}$  + *benzyl benzoate* (1:4422) (5);  $\bar{C}$  + *phenyl benzoate* (1:2257) (5);  $\bar{C}$  + *methyl cinnamate* (1:2090) (5);  $\bar{C}$  + *phenyl salicylate* ("Salol") (1:1415) (5); various others (5).

$\bar{C}$  with ethers:  $\bar{C}$  + *diethyl ether* (1:6110) (77);  $\bar{C}$  + *reratrole* (1:7560) (14).

$\bar{C}$  + compounds of Order 2.  $\bar{C}$  + *o-nitrophenol* (11);  $\bar{C}$  + *m-nitrophenol* (11);  $\bar{C}$  + *p-nitrophenol* (11);  $\bar{C}$  + *o-nitrobenzaldehyde* (7);  $\bar{C}$  + *m-nitrobenzaldehyde* (7);  $\bar{C}$  + *p-nitrobenzaldehyde* (7);  $\bar{C}$  + *nitropiperalonal* (7);  $\bar{C}$  + *azobenzene* (78);  $\bar{C}$  + *ethyl carbamate* (urethane) (16);  $\bar{C}$  + *urea* (78A).

BIOCHEMICAL ASPECTS OF  $\bar{C}$ 

[For study of toxicity of  $\bar{C}$  see (79); for study of bactericidal effect see (80) (81).]

PREPARATION OF  $\bar{C}$ 

From chloral (anhydrous). [For prepn. of  $\bar{C}$  from chloral (3:5210) by oxidn. with fung.  $\text{HNO}_3$  (82) (83) (84), with  $\text{HNO}_2$  (85), with  $\text{NO}_2$  at 40–60° (70% yield (86)), or with aq. chlorates + cat. see (312); for formn. of  $\bar{C}$  from chloral as by prod. of oxidn. with  $\text{O}_2$  see (23).]

From chloral hydrate. [For prepn. of  $\bar{C}$  from chloral hydrate (3:1270) by oxidn. with fung.  $\text{HNO}_3$  (63% yield (82)) (85), with  $\text{KMnO}_4$  (88), with  $\text{KClO}_3$  (89), with  $\text{Ca}(\text{OCl})_2$  (15), or with aq. chlorates + cat. (312) see indic. refs.]

From acetic acid. [For formn. (first discovery) of  $\bar{C}$  from acetic acid (1:1010) by chlorination with  $\text{Cl}_2$  in sunlight see (90).]

From tetrachloroethylene. [For formn. of  $\bar{C}$  from tetrachloroethylene (3:5460) by stdg. in aq. in light for 4 months see (91) cf. (92); for many other methods see text of tetrachloroethylene (3:5460) under oxidation.]

From miscellaneous sources. [For formn. of  $\bar{C}$  from pentachloroethyl chloroformate (Beil. III-13, III-1(6)) with aq. on htg. (93), but yield is small (94) owing to other modes of reaction (94); from pentachloroethyl trichloroacetate (Beil. II-210) with aq. (95); from trichloroacetyl chloride (3:5420) (96) or from trichloroacetic acid anhydride (3:6575) (97) (98) with aq.; from  $\beta,\beta,\beta$ -trichloroethyl alcohol (3:5775) by oxidn. with fung.  $\text{HNO}_3$  (210), see indic. refs.]

CHEMICAL BEHAVIOR OF  $\bar{C}$ PYROLYSIS OF  $\bar{C}$ 

(See also below under decarboxylation.) Pure  $\bar{C}$  shows no tendency to decompose at its b.p. (99). — [However,  $\bar{C}$  in presence of pumice begins to decompose about 180° giving (99)  $\text{HCl}$ ,  $\text{COCl}_2$  (3:5000),  $\text{CO} + \text{CO}_2$ . —  $\bar{C}$  in presence of  $\text{ThO}_2$  begins to decompose at 160–165° giving (99) the same products, although  $\bar{C}$  in presence of  $\text{ThO}_2$  above 210° (100) or in presence of kaolin above 230° (100) gives  $\text{CHCl}_3$  (3:5050), tetrachloroethylene (3:5460), hexachloroethane (3:4835),  $\text{HCl}$ ,  $\text{CO} + \text{CO}_2$ . —  $\bar{C}$  in presence of animal charcoal at 135° gives (99)  $\text{CHCl}_3$  (3:5050) +  $\text{CO}_2$ , but at 200–300° these are accompanied (100) by a little tetrachloroethylene (3:5460), hexachloroethane (3:4835),  $\text{HCl}$ , and  $\text{CO}$ . —  $\bar{C}$  at 300° in s.t. for 4 hrs. gives (101) trichloroacetyl chloride (3:5420),  $\text{CO}$ ,  $\text{CO}_2$  +  $\text{HCl}$ .]

REDUCTION OF  $\bar{C}$ 

[ $\bar{C}$  on partial reduction with  $\text{Zn} + \text{aq.}$  (102), with  $\text{Cu}$  powdr. in aq. (103), with  $\text{Cu}$  powdr. in  $\text{C}_6\text{H}_6$  + aniline (104) cf. (105), or  $\bar{C}$  on electrolytic reduction (106) gives (yields: 80% (103) (106), 75–85% (104)) dichloroacetic acid (3:6208).]

[ $\bar{C}$  on complete reduction with  $\text{HI}$  at 100° (87), or in aq. soln. with  $\text{K/Hg}$  (107) (84), or by electrolytic reduction with  $\text{Pt}$ ,  $\text{Cu}$ , or  $\text{Pb}$  electrodes (108) gives acetic acid (1:1010).]

[ $\bar{C}$  in aq. alc.  $\text{KOH}$  with  $\text{H}_2/\text{Pd}$  gives up all its chlorine as  $\text{HCl}$  (109) presumably yielding  $\text{AcOH}$  (1:1010).]

REACTIONS INVOLVING THE  $-\text{COOH}$  GROUP OF  $\bar{C}$ Decarboxylation of  $\bar{C}$ 

$\bar{C}$  in aq., in aq. alkalis, or in aniline or other organic bases undergoes cleavage into  $\text{CHCl}_3$  (3:5050) +  $\text{CO}_2$ ; for this decompn. presence of the trichloroacetate ion appears

necessary since in relatively nonbasic solvents it does not occur [e.g.,  $\bar{C}$  does not decompose at 25° in  $C_6H_6$  (110), toluene (111),  $CHCl_3$  (110) (111),  $CCl_4$  (110),  $CS_2$  (110), isoamyl alc. (117), acetone (110), ether (110), ethyl acetate (117), ethyl benzoate (110), acetic acid (117), nitrobenzene (110), or 6 *N*  $H_2SO_4$  (117); in MeOH (111) and in EtOH (111) (112) the only reaction is esterification (see below)].

The decompn. of  $\bar{C}$  into  $CHCl_3 + CO_2$  by boiling with nq. or nq. alk. has long been known (90) (113) (114) (115), and KCN behaves similarly (116). — [For studies on kinetics of decompn. of  $\bar{C}$  in aq. at various temps. see (4) (118) (119) (103) cf. (120); note that rate of decompn. is catalyzed by light (111) (119) (121) (122). — For studies of decompn. of aq. solns. of various salts (117) (123) (124) (125) and influence of light (126) (127) or of presence of various other inorganic salts (128) see indic. refs. — For studies of decompn. of  $\bar{C}$  in aqueous dioxane see (129). — Note that  $\bar{C}$  with  $Ca(OH)_2$  on htg. gives  $CHCl_3$  and that this reaction has been patented (134).]

[For study of decompn. of  $\bar{C}$  in aniline (117) (111) (130) (131) including influence of supersonic waves (132) see indic. refs.; for decompn. of  $\bar{C}$  in tertiary bases such as dimethylaniline see (133) but note in  $\bar{C}$  does not decompose in pyridine (111).]

[ $\bar{C}$  on htg. in resorcinol or cresol gives (135)  $CHCl_3 + CO_2$ , but  $\bar{C}$  on htg. in phenol or thymol decomposes differently yielding (135) (136) phosgene (3:5000) +  $HCl + CO$ .]

[Note that, as a consequence of the decompn. of  $\bar{C}$  into  $CHCl_3 + CO_2$ , it has been employed in Reimer-Tiemann types of condensation: e.g.,  $\bar{C}$  with phenol + aq. NaOH gives *o*-hydroxybenzaldehyde (1:0205) + *p*-hydroxybenzaldehyde (1:0060) (137) (138); many other phenols have also been studied (137) (138).]

### Acid Strength of $\bar{C}$

$\bar{C}$  in aq. soln. behaves as an exceedingly strong monobasic acid; Neut. Eq. = 163.4 (found 164.6 (91)). — [Ionization constant of  $\bar{C}$  in nq. soln. at 25° is about 1.2 (139) cf. (140), but because of strength of  $\bar{C}$  and its tendency to decompn. (see above) no accurate value is available (143). — For discussion of resonance and acid strength of  $\bar{C}$  see (141) (142) (143). — For studies of electrical conductivity of  $\bar{C}$  in aq. solns. at various temps. see (144) (145) (146) (147) (30).]

[Studies of acid strength of  $\bar{C}$  in nonaqueous solvents include the following: in EtOH (148) (149), in *n*-BuOH (150) (13), in ether (151), in  $CHCl_3$  (151), in formamide (152), in  $C_6H_6$  (153), in chlorobenzene (154), or in dioxane (155). — For study of electrometric titration of  $\bar{C}$  in  $C_6H_6$  (156), in ethylene glycol monomethyl ether ("methylcellosolve") (157), in anisole-*n* butyl alc. (157), see indic. refs. — For titration of  $\bar{C}$  in  $Ac_2O$  soln. with NaOAc see (158) cf. (310). — For study of behavior of  $\bar{C}$  with indicators in  $C_6H_6$  soln. see (159) (160).]

### Catalytic Effect of $\bar{C}$ on Various Reactions

The catalytic influence of  $\bar{C}$  upon diversified types of chem. reactions has been extensively examined; although this matter cannot be recorded exhaustively, the following examples are cited.

[For studies on catalytic effect of  $\bar{C}$  upon the inversion of *l*-menthone to *d*-isomenthone in  $C_6H_6$  (161) (162) or in chlorobenzene (163); upon racemization of methyl-phenyl-acetophenone and of isobutyl-phenyl-acetophenone in various solvents (164); of isopulegone to pulegone in nonaqueous solvents (165); or on hydrogen disproportionation of *d*-limonene (311), see indic. refs.]

[For studies of catalytic effect of  $\bar{C}$  upon the hydrolysis of EtOAc (144) or of sucrose (166) (167) see indic. refs.]

[For studies of catalytic effect of  $\bar{C}$  upon formn. of ether from EtOH (168); upon rate

of esterification of various org. acids in MeOH (159) or in EtOH (170); upon nitration of toluene (171) cf. (172); upon decompn. of ethyl diazoacetate in  $C_6H_6$  (162) or other solvents (173) (174) (175); upon decompn. of nitramide in iso-AmOH (176); upon rearr. of *N*-chloroacetanilide (177); upon rearr. of *N*-bromoacetanilide in chlorobenzene (178) (179) or in other solvents (179); upon rearr. of *N*-bromobenzanilide in chlorobenzene (180), upon chromate or perchlorate oxidn. of EtOH (181); upon addition of HBr to 3-methylbutene-1 (182), see indic. refs.

### Salts of $\tilde{C}$

This topic cannot here be treated exhaustively but the following examples are cited.

Salts with inorganic bases.  $[NH_4\tilde{A}]$ , prepn. (183),  $NH_4\tilde{A} \cdot \tilde{C}$  (184) (185);  $2NH_4\tilde{A} \cdot 5H_2O$  (186). — Hydroxylamine salt,  $HONH_2\tilde{A}$ , cryst. from dry ether by pptn. with lgr., m.p. 133–134° (187).]

$[Li\tilde{A}]$ ,  $n_D^{20}$  of aq. solns. (8), nonhygroscopic cpds. with betaine or pyridine betaine (188);  $Li\tilde{A} \cdot 2H_2O$  (189), conductivity of aq. solns (190). —  $Na\tilde{A}$  (198), effect of dry distillation (191), conductivity in aq. (190) (192), in dry MeOH (193), in dry EtOH (194);  $n_D^{20}$  of aq. solns. (8);  $Na\tilde{A} \cdot 3H_2O$  (196). —  $K\tilde{A} \cdot H_2O$  (189) (198), solubility and decompn. (197);  $K\tilde{A} \cdot \tilde{C}$  (184) (185).]

$[Ag\tilde{A}]$ , spar. sol. aq., darkens in air; on dry htg. decomposes above 80° (190) yielding (198)  $AgCl$ ,  $CO$ ,  $CO_2$ , and trichloroacetic acid anhydride (3 6575); with boilg. aq.  $Ag\tilde{A}$  yields (198)  $AgCl$ ,  $CO$ ,  $CO_2$ ,  $CHCl_3$  (3:5050), and  $\tilde{C}$ , for behavior of  $Ag\tilde{A}$  with  $I_2$  in  $C_6H_6$  see (200). —  $Hg\tilde{A}$ , ndls. from aq. in which it is spar. sol. (201) (202) (203) (209) (note that it is soluble in  $C_6H_6$  (202)). —  $Hg\tilde{A}_2$ , attempts to prepare this mercuric salt have been unsuccessful (201) (204); aq. solns. of  $\tilde{C}$  react with  $HgO$  long after theoretical amt. has been used (201), and  $CO$ ,  $CO_2$ , and  $CHCl_3$  are also formed (205).]

$[Mg\tilde{A} \cdot 4H_2O]$  (189). —  $Ca\tilde{A} \cdot 6H_2O$  (196);  $Ca\tilde{A}_2 \cdot 3\frac{1}{2}H_2O$ , eas. sol. (198). —  $Str\tilde{A}_2 \cdot 6H_2O$  (196). —  $Ba\tilde{A}_2 \cdot 6H_2O$  (196);  $Ba\tilde{A}_2 \cdot 2H_2O$  (206). —  $Be\tilde{A}_2 \cdot 2H_2O$  (207) (206). —  $Cd\tilde{A}_2$  (208);  $Cd\tilde{A}_2 \cdot 1\frac{1}{2}H_2O$  (217). —  $Zn\tilde{A}_2 \cdot 6H_2O$  (209). —  $Pb\tilde{A}_2 \cdot \frac{1}{2}H_2O$  (210);  $Ph\tilde{A}_2 \cdot H_2O$  (83). —  $Cu\tilde{A}_2 \cdot 6H_2O$  (83) (could not be confirmed (201) (211)),  $Cu\tilde{A}_2 \cdot 4H_2O$  (211);  $Cu\tilde{A}_2 \cdot 3H_2O$  (201) (complexes with benzylamine (212));  $Cu\tilde{A}_2 \cdot 2H_2O$  (complexes with various amines (213));  $Cu\tilde{A}_2$  (201) (complexes with various amines (213) (214)), electrolysis (215), electrometric titration (216).]

$[Mn\tilde{A}_2 \cdot 3\frac{1}{2}H_2O]$  (217). —  $Co\tilde{A}_2 \cdot 4H_2O$  (218) (complexes with various amines (218) (219));  $Co\tilde{A}_2 \cdot 3\frac{1}{2}H_2O$  (217). —  $Ni\tilde{A}_2 \cdot 4H_2O$  (189) (218) (complexes with  $NH_3$  (211) and various amines (220)).]

Salts with organic bases. [*Aniline trichloroacetate*, from  $\tilde{C}$  (1 mole) + aniline (1 mole) in  $C_6H_6$  (223) (224), or without solvent (225), or in aq. (226); this salt has no true m.p. (224) although various values ranging from 145° (226) to 163° (225) have been reported. — Note that, although action of heat would be expected to cause loss of  $H_2O$  giving  $\omega,\omega,\omega$ -trichloroacetanilide (see below), no actual study has been reported. — Note that  $\tilde{C}$  + aniline + Cu powder in  $C_6H_6$  soln. gives dichloroacetic acid (3 6208) (75–85% yield (223) cf. (227)). — Note finally the existence of an acid salt of  $\tilde{C}$  with aniline, m.p. 107–108° (221), from  $\tilde{C}$  (2 moles) with aniline (1 mole). — *o*-Toluidine trichloroacetate; the prepn. of this salt, m.p. 167–168° dec. (225), has been claimed (225) but could not be confirmed (221) (225); no other record of it can be found. — *p*-Toluidine trichloroacetate; the prepn. of this salt, m.p. 135° dec. (225), has been claimed (225) but could not be confirmed (221) (225); no other record of it can be found. — *N*-Methylaniline trichloroacetate; m.p. 97° (225).]

*o*-Phenylethylamine trichloroacetate: unreported. — Benzylamine trichloroacetate: from  $\tilde{C}$  + benzylamine in EtOAc, m.p. 118.8–119.5° u c, 120.3–121.3° cor. (229) (note that this

m.p. is practically identical with corresp. benzylamine salt of chloroacetic acid (3:1370) q.v.). — *Piperazine bis-(trichloroacetate)*, m.p. 121.0–121.5° car. (230). — *Semicarbazide trichloroacetate*: m.p. 154° dec. (231).

[*Phenylhydrazine trichloroacetate*: from  $\bar{C}$  with phenylhydrazine in  $C_6H_6$ , m.p. 123° (232). (Note that this product is definitely the salt since on titration with alk. it gives Neut. Eq. 204.7 as against a calcd. value of 202.6 (232); this salt upon htg. would be expected to lose  $H_2O$  giving trichloroacetophenylhydrazide, but this product is unreported.)]

[For salts of  $\bar{C}$  with *o*-, *m*-, and *p*-phenylenediamines see (233).]

### Behavior of $\bar{C}$ with Metals

[ $\bar{C}$  with aq. + Zn wool (102), or  $\bar{C}$  with Cu powder in aq. or  $C_6H_6$  (223) (103) (227), gives dichloroacetic acid (3:6208) q.v. —  $\bar{C}$  in conc.  $NH_4OH$  dissolves Cu, Zn, or Cd with strong evolu. of  $H_2$  but does not attack Ag (234)]

### Esterification of $\bar{C}$

This book includes the following esters of  $\bar{C}$  under their own individual numbers, q.v.: *methyl trichloroacetate* (3:5500), *ethyl trichloroacetate* (3:5950), *n-propyl trichloroacetate* (3:6135), *isopropyl trichloroacetate* (3:5975), *n-butyl trichloroacetate* (3:6315), *isobutyl trichloroacetate* (3:6140), *sec-butyl trichloroacetate* (3:9372), *ter-butyl trichloroacetate* (3:0138), *n-amyl trichloroacetate* (3:6560), *isoamyl trichloroacetate* (3:6400), *ter-amyl trichloroacetate* (3:6185), *trichloromethyl trichloroacetate* (3:0290),  *$\beta$ -chloroethyl trichloroacetate* (3:6510), and  *$\beta$ -methoxyethyl trichloroacetate* (3:9250).

[For studies on esterification of  $\bar{C}$  under various conditions with MeOH (1:6120) (235) (236), with EtOH (1:6130) (235) (237) (238) (239) (240) (241) (242) (243) (244) (20), with *n*-propyl alc. (1:6150) (245), with isopropyl alc. (1:6135) (245) (240) (238), with *n*-butyl alc. (1:6180) (247) (248), with isobutyl alc. (1:6165) (247) (248) (83), with *sec*-butyl alc. (1:6155) (247), with *ter*-butyl alc. (1:6140) (238), with *n*-amyl alc. (1:6205) (248), with pentanol-2 (1:6185) (248), with pentanol-3 (1:6175) (248), with *ter*-amyl alc. (1:6160) (248), with neopentyl alc. (1:5812) (249), with methyl-vinyl-carbinol (250), with benzyl alc. (1:6480) (238) (251), with diphenylcarbinol (1:5960) (238), with triphenylcarbinol (1:5985) (238), see indic. refs.]

[For study of equilibrium of transesterification with MeOAc (1:3005) or with EtOAc (1:3015) at 30° see (21).]

### Addition Reactions of $\bar{C}$ with Organic Compounds

**Addition to unsaturated linkages.**  $\bar{C}$  in pres. of suitable catalysts adds to unsatd. linkages giving the corresp. esters [e.g.,  $\bar{C}$  with propylene +  $BF_3$  gives (48.8% yield (246)) isopropyl trichloroacetate (3:5975);  $\bar{C}$  with trimethylethylene (2-methylbutene-2) (1:8220) gives both *ter*-amyl trichloroacetate (3:6185) and methyl-isopropyl-carbinyl trichloroacetate (for extensive studies of this reaction see (252) (253) (254) (255) (256) (257) (258) (259) (260))].

[ $\bar{C}$  with acetylene +  $HgSO_4$  at 60–80° gives (261) vinyl trichloroacetate [Beil. II-(94)], b.p. 149° at 760 mm.]

**Addition to epoxy compounds.** [ $\bar{C}$  with ethylene oxide (1:6105) in cold gives (28% yield (262)) (263) (264) ethylene glycol (mono)trichloroacetate ( $\beta$ -hydroxyethyl trichloroacetate) (3:9099). — For behavior of  $\bar{C}$  with 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358) see (264).]

• Conversion of  $\bar{C}$  to Corresponding Acid Halides

[The corresponding trichloroacetyl fluoride is unreported.]

[ $\bar{C}$  with  $PCl_3$  (266) (268) (269), with  $PCl_2 + ZnCl_2$  (25% yield (270)), with  $SOCl_2$  (yield 12% (270), 30% (271)) in  $C_6H_6$  (60% yield (272)) or in pyridine (90% yield (273)), with  $P_2O_5 + HCl$  gas (274), with benzotrichloride (3:6340) +  $ZnCl_2$  at  $100^\circ$  (77% yield (275)), or with benzoyl chloride (3:6240) (51–56% yield (276)) gives trichloroacetyl chloride (3:5420). — Note also that  $\bar{C}$  on pyrolysis at  $300^\circ$  decomposes (100) with formn. of  $CO_2 + CO_2 +$  trichloroacetyl chloride (3:5420) +  $HCl$ .]

[ $\bar{C}$  with  $PBr_3$  gives (265) (266) trichloroacetyl bromide, b.p.  $143^\circ$  (266),  $139.5\text{--}140^\circ$  (265); this product is also obt'd. from trichloroacetyl chloride (3:5420) with  $HBr$  gas at  $-5^\circ$  (70% yield (267)).]

[ $\bar{C}$  with  $PI_3$  (266) (or better trichloroacetyl chloride (3:5420) with  $HI$  at  $-5^\circ$  (277)) gives (71.5% yield (277)) trichloroacetyl iodide, b.p.  $74.0\text{--}74.2^\circ$  at 30 mm. (277).]

Conversion of  $\bar{C}$  to Corresponding Anhydride

[ $\bar{C}$  with  $P_2O_5$  at  $200\text{--}215^\circ$  (278) (279), or  $Na\bar{A}$  with  $SO_2Cl_2$  (or  $SO_2 + Cl_2$ ) in  $EtOAc$  (280), or  $\bar{C}$  with trichloroacetyl chloride (3:5420) and  $PCl_3$  (281),  $P_2O_5$  (282), or  $AlCl_3$  (283) gives (yields: 90–95% (280), 80% (278)) trichloroacetic acid anhydride (3:6575).]

Ⓐ Color test with  $NH_4OH/Cu_2Cl_2$  reagent.  $\bar{C}$  on shaking in filled stoppered bottle with conc. aq.  $NH_4OH$  contg.  $Cu_2Cl_2$  gives dark blue color instantly (284); note, however, that very similar behavior is shown by dichloroacetic acid (3:6208).

— Methyl trichloroacetate: oil, b.p.  $153^\circ$  (see 3:5800).

— Ethyl trichloroacetate: oil, b.p.  $167^\circ$  (see 3:5950).

— Phenyl trichloroacetate: oil, b.p.  $254\text{--}255^\circ$  dec. (135). [From trichloroacetyl chloride (3:5420) with sodium phenolate in pet. ether (135).] [Note that the isomeric 4-(trichloroacetyl)phenol, m.p.  $99.0\text{--}99.5^\circ$  has been prep'd. indirectly from trichloroacetonitrile + phenol +  $AlCl_3$  (285).]

— o-Tolyl trichloroacetate: unreported [Note, however, that the isomeric 4-(trichloroacetyl)-2-methylphenol, m.p.  $90\text{--}91^\circ$ , has been obt'd. indirectly (285).]

— m-Tolyl trichloroacetate: unreported. [Note, however, that both the isomers, viz., 4-(trichloroacetyl)-3-methylphenol, m.p.  $83\text{--}87^\circ$ , and 6-(trichloroacetyl)-3-methylphenol, oil, have been obt'd. indirectly (285).]

— p-Tolyl trichloroacetate: m.p.  $68\text{--}69^\circ$  (285). [Obtd. only by indirect means (285).]

— Benzyl trichloroacetate: oil, b.p.  $178.5^\circ$  at 50 mm (286),  $148\text{--}149^\circ$  at 15 mm. (264),  $D_4^{25} = 1.3887$  (286),  $n_D^{18} = 1.5288$  (286). [From  $\bar{C}$  with benzyl alc. (1:6480) +  $HCl$  gas at  $100^\circ$  (286), or from trichloroacetyl chloride (3:5420) with benzyl alc (1:6480).]

— p-Nitrobenzyl trichloroacetate: m.p. about  $80^\circ$  cf. (287). [Unsuitable as Ⓐ (287).]

— Phenacyl trichloroacetate: unreported.

— p-Chlorophenacyl trichloroacetate: unreported.

— p-Bromophenacyl trichloroacetate: unreported.

— p-Iodophenacyl trichloroacetate: unreported.

— p-Phenylphenacyl trichloroacetate: unreported.

Ⓐ S-Benzylthiuronium trichloroacetate: m.p.  $148\text{--}149^\circ$  (288). [Note that for corresp. salts from chloroacetic acid (3:1370) and from dichloroacetic acid (3:6208) m.p. values are respectively  $159\text{--}160^\circ$  and  $178\text{--}179^\circ$  (288).]

Ⓐ S-(p-Chlorobenzyl)thiuronium trichloroacetate: m.p.  $148^\circ$  cor. (289). (From  $\bar{C}$  (as  $Na\bar{A}$ ) with S-(p-chlorobenzyl)thiuronium chloride (289) (m.p.  $197^\circ$ ) in alc. (289); note that corresp. deriv. of chloroacetic acid (3:1370) has m.p.  $158^\circ$  cor. (289).]

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## 3:1160 2,3,6-TRICHLOROPHENOL



Beil. VI - 190

VI<sub>r</sub>—VI<sub>r</sub>—(180)

M.P. 58° (1) (2)

B.P. 252-253° u.c. (5)

55° (4)

248.5-249.5° (6)

53-54° (5) (6)

Ndls. (from alc.) with intense and persistent phenolic odor. — Somewhat sol. in hot aq.; volatile with steam. — Eas. sol. alc., ether, lgr., AcOH; sol. hot  $C_6H_6$  but ppts. on cooling.

[For prepn. from 2,3,6-trichloro-4-aminophenol via diazo reactn. see (3).]

$\bar{C}$  is strongly acidic; iocization const. at 25° is  $7.3 \times 10^{-7}$  (2);  $\bar{C}$  dissolves in  $Na_2CO_3$  or NaOH (5);  $\bar{C}$  can be titrated with  $N/10$  alk.; Neut. Eq. = 197.5 (1) (4).

$\bar{C}$  in AcOH, treated with 1.4 moles  $Br_2$ , poured into aq. yields 4-bromo-2,3,6-trichlorophenol, ndls. from AcOH, m.p. 80° (3). [The methyl ether of this prod. has m.p. 69-70°; the benzoate, m.p. 110° (3).]

$\bar{C}$  treated with 1.5 moles  $Br_2$  without solvent yields (3) 4,5-dibromo-2,3,6-trichlorophenol, ndls. from dil. AcOH, m.p. 205° (3). [The methyl ether of this prod. has m.p. 130°; the benzoate, m.p. 153° (3).]

$\bar{C}$  treated with  $(CH_3)_2SO_4$  + 20% KOH at 100° for an hour yields its own methyl ether, 2,3,6-trichloroanisole, h.p. 227-229° at 756 mm.; pr. from alc., m.p. 45° (3).

Ⓢ 2,3,6-Trichlorophenyl benzoate: from  $\bar{C}$  +  $BzCl$  + 10% KOH; cryst. from pet. ether/lgr., m.p. 92-93° (3); from alc., m.p. 90° (4).

3:1160 (1) Tiessens, *Rec. trav. chim.* **50**, 113-114 (1931). (2) Tiessens, *Rec. trav. chim.* **48**, 1066-1068 (1929). (3) Kohn, Fink, *Monatsh.* **56**, 139-141 (1930). (4) Holleman, *Rec. trav. chim.* **52**, 742-743 (1920). (5) Lampert, *J. prakt. Chem.* (2) **33**, 376-378 (1886). (6) Hirsch, *Ber.* **13**, 1908 (1880).

## 3:1175 2,3-DICHLOROPHENOL



Beil. VI —

VI<sub>r</sub>—(102)VI<sub>r</sub>—

M.P. 58° (1)

B.P. 206° (1)

56-57° (2) (3)

Cryst. (from pet. eth. (3)). —  $\bar{C}$  mixed with 2,5-dichlorophenol (3:1190), m.p. 57°, depresses m.p. (2). —  $\bar{C}$  is extraordinarily volatile; if dried in vac. this leads to substantial

losses; the volatility and intense odor of  $\bar{C}$  differentiate this dichlorophenol from its isomerides (2). — Odor resembles that of *o*-chlorophenol and iodoform (3). —  $\bar{C}$  is volatile with steam (3).

[For prepn. from 3-amino-2-chlorophenol via Sandmeyer method see (2) (4); from 2,3-dichloroaniline via diazo reaction see (3); from barium 2,3-dichlorophenol-4,6-disulfonate by hydrolysis of sulfonic acid groups with steam (70% yield) see (1).]

[For data on dissociation constant see (5).]

$\bar{C}$  on direct bromination (1) yields 4,6-dibromo-2,3-dichlorophenol, colorless ndls. (rapidly becoming opaque) from AcOH (1), or colorless feathery ndls. from alc. (4), m p. 90° (1) (4). [The methyl ether of this product, 4,6-dibromo-2,3-dichloroanisole, long needle-like pr. from alc., has m.p. 82° (1).]

$\bar{C}$  dislvd. in aq. NaOH and shaken with  $(CH_3)_2SO_4$  yields (3) the methyl ether, 2,3-dichloroanisole, m.p. 31° (3).

3:1175 (1) Hodgson, Kershaw, *J. Chem. Soc.* 1930, 1423. (2) Henley, Turner, *J. Chem. Soc.* 1930, 940. (3) Holleman, *Rec. trav. chim.* 37, 101-104 (1918). (4) Hodgson, Smith, *J. Chem. Soc.* 1931, 2271. (5) Murray, Gordon, *J. Am. Chem. Soc.* 57, 110-111 (1935).

### 3:1190 2,5-DICHLOROPHENOL



$C_6H_4OCl_2$

Beil. VI - 189

VI<sub>1</sub>-(103)

VI<sub>2</sub>-(178)

M.P. 58° (1) (2) (3) (4)  
59° (5)

B.P. 211° at 744 mm. (1) (4)  
94° at 14 mm. (3)

Cryst with strong and persistent phenolic odor. — Spar. sol. aq., eas. sol. alc., ether,  $C_6H_6$  — Volatile with steam.

[For prepn. from 2,5-dichloroaniline [Beil. XII-625] via diazo reaction (90% yield (1); 86% yield (6); 70% yield (5)) see (1) (6) (5) (2); from 1,2,4-trichlorobenzene + NaOCH<sub>3</sub> in MeOH at 180° see (7) ]

$\bar{C}$  in dil. alc. reddens blue litmus, dec. on boilg. with Na<sub>2</sub>CO<sub>3</sub>. Gives only faint color with FeCl<sub>3</sub> (1). [For study of ionization const. see (11) ]

$\bar{C}$  dislvd. in 3 pts. CHCl<sub>3</sub> and shaken with conc. HNO<sub>3</sub> gives on cooling CHCl<sub>3</sub> 80% yield of 2,5-dichloro-4-nitrophenol [Beil. VI-241], colorless ndls. from pet ether, m p. 117° (8). [Further nitration yields 2,5-dichloro-4,6-dinitrophenol, yel. pr. m p. 146° (8).] —  $\bar{C}$  htd. with conc. H<sub>2</sub>SO<sub>4</sub> + fumg. H<sub>2</sub>SO<sub>4</sub>, then nitrated as specified (9), yields 2,5-dichloro-6-nitrophenol, volatile with steam, yel. pr. from pet. eth., m p. 70° (9).

$\bar{C}$  in AcOH treated with 2 moles Br<sub>2</sub>, poured into nq., gives (100% yield (6)) 2,5-dichloro-4,6-dibromophenol, ndls. from dil. AcOH, m.p. 100.5° (6), 99-100° (10). [This dibromo compd. results also from  $\bar{C}$  in AcOH + NaOAc + 1 mole Br<sub>2</sub> on htg. at 100° (10).] [ $\bar{C}$  with Fe + excess Br<sub>2</sub> gives (100% yield (6)) 2,5-dichloro-3,4,5-tribromophenol, ndls. from AcOH, m p. 206° (6).]

$\bar{C}$  dislvd. in KOH and shaken with  $(CH_3)_2SO_4$  yields the methyl ether, 2,5-dichloroanisole, b p 225-227° u c. at 752 mm. (6), b p. 140° at 40 mm. (2), m p. 24° (5) (2).

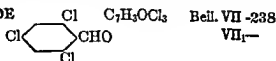
③ 2,5-Dichlorophenyl benzoate: from  $\bar{C}$  + aq. KOH + BzCl, ndls. from 96% alc., m p. 69° (6).

3:1190 (1) Noeltling, Kopp, *Ber.* 38, 3510 (1905). (2) Holleman, *Rec. trav. chim.* 37, 101-104 (1918). (3) Kohlrausch, Stockmair, Ypsilanti, *Monatsh.* 67, 90 (1936). (4) Ger. 349,794, March 9, 1922; *Cent.* 1922, IV 45. (5) de Crauw, *Rec. trav. chim.* 50, 770 (1931). (6) Kohn, Fink, *Monatsh.* 58, 78-83 (1931). (7) Holleman, *Rec. trav. chim.* 37, 201 (1918). (8) Fries, *Ann.* 454,

247 (1927). (9) Hodgson, Kershaw, *J. Chem. Soc.* 1029, 2922-2923. (10) Fox, Turner, *J. Chem. Soc.* 1930, 1860.

(11) Murray, Gordon, *J. Am. Chem. Soc.* 57, 110-111 (1935).

### 3:1200 2,4,6-TRICHLOROBENZALDEHYDE



M.P. 58-50° (1) (2)

Cryst. from lgr.

[For prepn. of  $\bar{C}$  from 2,4,6-trichlorobenzal (di)chloride (3:0142) by hydrolysis with fung.  $H_2SO_4$  (94% yield) see (1); for prepn. of  $\bar{C}$  from 4-amino-2,6-dichlorobenzaldehyde by diazotization and use of  $Cu_2Cl_2$  reaction see (1).]

[ $\bar{C}$  on oxidn. with  $KMnO_4$  should yield 2,4,6-trichlorobenzoic acid (3:4545), m.p. 164°, but this reaction is not actually reported in the literature.]

$\bar{C}$  with 50% aq.  $KOH$  or 50% aq.  $NaOH$  at 100° undergoes cleavage of the aldehyde group giving (yields: 89% and 74% respectively) 1,3,5-trichlorobenzene (3:1400), m.p. 63°, accompanied by the corresp. potassium formate (1).

[ $\bar{C}$  with  $MeMgI$  in dry ether, followed by usual hydrolysis, gives (93% yield (3)) methyl-2,4,6-trichlorophenyl-carbinol, ndls. from lgr., m.p. 76.5°, b.p. 158-163° cor. at 17 mm.]

— 2,4,6-Trichlorobenzaldehyde: unreported.

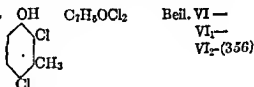
— 2,4,6-Trichlorobenzaldehyde phenylhydrazone: unreported.

— 2,4,6-Trichlorobenzaldehyde *p*-nitrophenylhydrazone: unreported.

— 2,4,6-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

3:1200 (1) Lock, *Ber.* 66, 1532 (1933). (2) Geigy & Co. Ger. 199,943, July 4, 1908; *Cent.* 1903, II 303-304; [*C.A.* 2, 3000 (1908)]. (3) Lock, Böck, *Ber.* 70, 924 (1937).

### 3:1205 2,4-DICHLORO-3-METHYLPHENOL (2,4-Dichloro-*m*-cresol.)



M.P. 58-59° (1) B.P. 235-236° at 745 mm. (2)

58° (2) 234° (1)

75-80° at 4 mm. (1)

Note that the products of m.p. 44° (3), 45° (4), and 46° (5) formerly supposed to have been  $\bar{C}$  are now regarded (1) as 2,4,6-trichloro-3-methylphenol (3:0618).

[For prepn. of  $\bar{C}$  from 2-chloro-3-methylphenol (3:1055) or from 4-chloro-3-methylphenol (3:1535) in cold  $CHCl_3$  with  $Cl_2$  see (1); from 3-methylphenol (*m*-cresol) (1:1730) in  $CHCl_3$  with 2 moles  $Cl_2$  (other isomers are also formed) see (1); from 3-methylphenol-sulfonic acid-4 (2) in nitrobenzene solution with  $Cl_2$  (other products are also formed) see (2).]

$\bar{C}$  in  $CHCl_3$  gives with  $Cl_2$  (1 mole) alm. quant. yield (1) 2,4,6-trichloro-3-methylphenol (3:0618), m.p. 46° (1).

$\bar{C}$  in  $CHCl_3$  gives with  $Br_2$  (1 mole) (1) 2,4-dichloro-6-bromo-3-methylphenol, m.p. 58-59° (1).

Ⓐ 2,4-dichloro-3-methylphenyl benzoate: fine plates from alc., m.p. 78-78.5° (1)  
[From  $\bar{C}$  with  $BzCl$  in pyridine (1).]

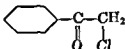
② 2,4-Dichloro-3-methylphenyl benzenesulfonate: fine ndl.-like pl. from alc., m.p. 69.5° (1). [From  $\bar{C}$  with benzenesulfonyl chloride in pyridine (1).] [Note the proximity of the m.p. of this deriv. to that of the corresp. deriv. of 2,6-dichloro-3-methylphenol (3:0618).]

③ 2,4-Dichloro-3-methylphenyl *p*-toluenesulfonate: shiny pl. from alc., m.p. 100-101° (1). [From  $\bar{C}$  with *p*-toluenesulfonyl chloride in pyridine (1).]

(5) Claus, Schweitzer, *Ber.* 19, 930 (1886). 4216-4218 (1933). (2) Huston, Neely, *J. Am. Chem. Soc.* 51, 275-276 (1929). (3) Mitter, *J. Am. Chem. Soc.* 41, 2033 (1919).

### 3:1212 PHENACYL CHLORIDE

( $\alpha$ -Chloroacetophenone,  
 $\omega$ -chloroacetophenone,  
chloromethyl phenyl ketone)



$C_8H_7OCl$

Beil. VII - 282  
VII-1 (151)

M.P. 60°	(1)	B.P. 244-245°	u.c.	(6)
59°	(2)	244°		(37)
58-59°	(3) (4) (5) (6)	241-242°		(36)
58.8°	(7)	140°	at 15 mm.	(1)
58.5°	(8)	139-141°	at 14 mm.	(3)
57-58°	(9) (71)	120.0-120.2°	at 10 mm.	(12)
57°	(10) (11)	120-125°	at 4 mm.	(15)
56.5-56.8°	(12)			
56.5°	(13) (14)			
56-57°	(15) (64)			
56°	(16) (36)			
55-55.5°	(17)			
55°	(37)			
54.5°	(18) (154)			
54°	(31)			

Colorless tcls. from dil. alc. or lgr. — Vapors of  $\bar{C}$  are very strongly lachrymatory (see also below). —  $\bar{C}$  is insol. aq. but volatile with steam;  $\bar{C}$  is cas sol. alc., ether, or  $C_6H_6$ .

[For study of soly. of  $\bar{C}$  in EtOH,  $C_6H_6$ ,  $CCl_4$ , or acetophenone over range -23.5° to 53.5° see (19): note that  $\bar{C}$  with  $C_6H_6$  (1:7400) gives (19) a eutectic, m.p. -1.6°, contg. 76 wt. %  $\bar{C}$ ;  $\bar{C}$  with acetophenone (1:5515) gives a eutectic, m.p. +5.9°, contg. 70 wt. %  $\bar{C}$  (19).]

### USES OF $\bar{C}$

In addn. to its uses as a chem. intermediate,  $\bar{C}$  because of its irritant and lachrymatory properties has been much studied as a chemical warfare agent and tear gas under the arbitrary designation "CN."

[For general surveys from this viewpoint see (20) (21). —  $\bar{C}$  is sol. in many org. solvents and is frequently loaded into grenades and shells in such solutions of which three common examples are "CNB" (consisting of  $\bar{C}$  +  $C_6H_6$  +  $CCl_4$ ), "CND" (consisting of  $\bar{C}$  + ethylene dichloride (3:5130)), and "CNS" (consisting of  $\bar{C}$  +  $CHCl_3$  + nitrochloroform = chloropicrin). — For examples of patents on these and other types of tear-gas cartridges and munitions coatg.  $\bar{C}$  see (23) (24) (25) (26) (27); for use of  $\bar{C}$  as insecticide see (28).]

[For dispensing apparatus for  $\bar{C}$  (29) or for mill for disintegration of  $\bar{C}$  (30) see indic. refs.]

[For m.p./compn. diagram of system  $\bar{C}$  + "Adamsite" (10-chloro-9,10-dihydrophenarsazine), eutectic, m.p. 50°, contg. 90 mole %  $\bar{C}$ , see (31).]

[For studies of effect of  $\bar{C}$  on skin see (32) (33) (34); for contamination of food by  $\bar{C}$  see (35).]

### PREPARATION OF $\bar{C}$

From chloroacetyl chloride with benzene. [For prepn. of  $\bar{C}$  from chloroacetyl chloride (3:5235) with  $C_6H_6 + AlCl_3$  (yield 85–88% (15) (64)) (2) (14) (36) (71) see indic. refs.]

From acetophenone. [For prepn. of  $\bar{C}$  from acetophenone (1:5515) with  $Cl_2$  in AcOH (4) (18), in  $CS_2$  (85% yield (37)), in lgr. (38) or directly without solvent (yields 65% (6) (37)) (39) see indic. refs.; from acetophenone (1:5515) by electrolysis of its soln. in HCl (40), or by chlorination with aq. *N*-chlorosuccinimide (41), see indic. refs.]

From benzoyl chloride with diazomethane. [For formn. of  $\bar{C}$  from benzoyl chloride (3:6240) with diazomethane in ether (72% yield) see (3); note, however, that this procedure has subsequently been much disputed, and for discussion see also (42) (43) (44) (45) (46) (47) (48).]

From miscellaneous sources. [For prepn. of  $\bar{C}$  from *N*-( $\alpha,\beta$ -dichlorovinyl)diethylamine (yield 92.6% (49)), from chloroacetonitrile (50), or for possible formn. from chloroacetic acid (3:1370) (51), all with  $C_6H_5MgBr$ , see indic. refs.; for formn. of  $\bar{C}$  from phenyl copper (52), from phenyldichloroarsine (yields: 58.5% (53), 55% (54)) (55), all with chloroacetyl chloride (3:5235), see indic. refs.; for formn. of  $\bar{C}$  from 1-chloro-2-phenylpropanol-2 (styrene chlorohydrin) (3:9570) by oxidn. with  $K_2Cr_2O_7/H_2SO_4$  (1) or from diphenacyltelluride dichloride by oxidn. with  $KMnO_4$  (5) see indic. refs.; for formn. of  $\bar{C}$  from benzalacetophenone (chalcone) (1:5155) by actn. of  $Cl_2$  in *tert*-butyl alc. (other prods. are also formed) see (17).]

### CHEMICAL BEHAVIOR OF $\bar{C}$

#### REDUCTION

No authentic studies on reduction of  $\bar{C}$  appear to be reported.

#### OXIDATION

$\bar{C}$  on oxidn. with  $CrO_3$  (39), or  $K_2Cr_2O_7 + H_2SO_4$  (58) (13) gives benzoic acid (1:0715). —  $\bar{C}$  also reduces  $NH_4OH/AgNO_3$  (13) [perhaps because of some hydrolysis to  $\omega$ -hydroxyacetophenone (1:5180)].

#### HALOGENATION

Chlorination. [ $\bar{C}$  on further chlorination under conditions favoring side-chain substitution would be expected to yield  $\omega,\omega$ -dichloroacetophenone (3:6835) and ultimately  $\omega,\omega,\omega$ -trichloroacetophenone (3:6874), but no authentic record that this has actually been achieved can be found.]

Bromination. [ $\bar{C}$  with  $Br_2$  under suitable conditions gives (56)  $\omega$ -bromo- $\omega$ -chloroacetophenone, m.p. 37–37.5°, b.p. 133–134° at 7.5 mm. (56). —  $\bar{C}$  in AcOH + NaOAc with  $Br_2$  as directed (57) gives a mixt. consisting of 30%  $\omega,\omega$ -dibromo- $\omega$ -chloroacetophenone + 70%  $\omega,\omega,\omega$ -tribromoacetophenone.]

Nitration.  $\bar{C}$  in conc.  $H_2SO_4$  at  $-20^\circ$  treated as directed (9) with a mixt. of fuming  $HNO_3$  ( $D = 1.50$ ) + conc.  $H_2SO_4$  gives (77% yield (9)) *m*-nitrophenacyl chloride, m.p. 103° (59), 102–103° (16), 100.5–102° (9). — [Note that the other two isomeric mononitrophenacyl chlorides, viz., *o*-nitrophenacyl chloride, m.p. 66–67° (60) (61), and *p*-nitrophenacyl chloride, m.p. 107° (62), are also known, but prepd. indirectly; note also that no dinitration prods. of  $\bar{C}$  are known.]

### BEHAVIOR OF $\bar{C}$ WITH OTHER INORGANIC REACTANTS

With water.  $\bar{C}$  does not readily hydrolyze with aq. but on protracted boilg. (e.g., 20 hrs. (63)) with a large vol. of aq. gives  $\omega$ -hydroxyacetophenone (1:5180).]

With nitrous acid.  $\bar{C}$  with  $\text{HNO}_2$  (from *n*-butyl nitrite +  $\text{HCl}$  gas) in dry ether gives (yields: 85.6% (64), 82–86% (15))  $\omega$ -chloro- $\omega$ -isonitrosoacetophenone (phenylglyoxylohydroxamyl chloride) [Beil. X-662,  $X_1$ -(315)], white ndls. from  $\text{CCl}_4$  (64) or from  $\text{CCl}_4$  +  $\text{C}_6\text{H}_6$  (3:1) (15), m.p. 132–133° (15) (64).

With  $\text{PCl}_5$ .  $\bar{C}$  with  $\text{PCl}_5$  on distn. gives (65)  $\alpha,\beta$ -dichlorovinylbenzene ( $\alpha,\beta$ -dichlorostyrene) [Beil. Y-477,  $V_2$ -(367)], b.p. 221°.]

With various salts of inorganic acids.  $\bar{C}$  with  $\text{KI}$  (66) (67) or better  $\text{NaI}$  (38) in alc. gives  $\omega$ -iodoacetophenone (phenacyl iodide) [Beil. VII-286], m.p. 30°; for study of rate of reactn. of  $\bar{C}$  with  $\text{KI}$  in acetone at 0° (11) or with  $\text{NaI}$  or  $\text{LiI}$  in acetone at 0° or –10° (10) see indic. refs.]

$\bar{C}$  does not add  $\text{NaHSO}_3$  (37). —  $\bar{C}$  in alc. with  $\text{Na}_2\text{S}_2\text{O}_3$  (2 moles) in aq. refluxed 20 hrs. gives sodium phenacylthiosulfate which with  $\text{HCl}$  gives (73% yield (69))  $\omega$ -mercaptoacetophenone (phenacyl mercaptan). —  $\bar{C}$  with  $\text{Na}_2\text{S}$  in alc. at 60° gives (70) diphenacyl sulfide [Beil. VIII-94, VIII<sub>1</sub>-(541)], m.p. 76.5–77.2° (70), 76° (147); for use of this reactn. in detn. of  $\bar{C}$  see (14).

With ammonia.  $\bar{C}$  with  $\text{NH}_3$  (1 mole) would be expected to give  $\omega$ -aminoacetophenone (phenacylamino) [Beil. XIV-49, XIV<sub>1</sub>-(368)], but such direct result has never been reported; note, however, that  $\bar{C}$  (1 mole) with hexamethylenetetramine (1 mole) in  $\text{CHCl}_3$  at room temp. for 12 hrs. gives (60% yield (68)) a 1:1 addn. cpd., m.p. 145°, which upon alcoholysis with conc.  $\text{HCl}$  in alc. 3 days in cold gives (63–74% yield (68)) phenacylamino hydrochloride.

$\bar{C}$  with alc.  $\text{NH}_3$  in s.t. at 100° as directed (2) gives a mixt. contg. diphenacylamino hydrochloride [Beil. XIV-53, XIV<sub>1</sub>-(371)], m.p. 235°, together with the hydrochlorides of 2,5-diphenylpyrazine and 2,6-diphenylpyrazine; for discussion of mechanism see (2).]

### BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

#### With Hydrocarbons (+ $\text{AlCl}_3$ )

$\bar{C}$  with  $\text{C}_6\text{H}_6$  +  $\text{AlCl}_3$  in s.t. at 100° failed to react (71). —  $\bar{C}$  with toluene (1:7405) +  $\text{AlCl}_3$  under reflux gives (71) a prod., m.p. 84–85°, which is presumably  $\omega$ -(*p*-tolyl)acetophenone [Beil. VII-448], although this prod. obtd. by other methods has different consts.

#### With Organic Hydroxy (or Mercapto) Compounds

With alcohols.  $\bar{C}$  with  $\text{NaOMe}$  might be expected to yield  $\omega$ -methoxyacetophenone, b.p. 228–230° at 760 mm. (72) (73), b.p. 118–120° at 15 mm. (72) (73), m.p. 7–7.5° (73) (corresp. semicarbazone, m.p. 85° (72), 129° (73) (note disagreement); corresp. 2,4-dinitrophenylhydrazones, m.p. 191–192° (73)); note, however, that no record of this reaction has been reported and the  $\omega$ -methoxyacetophenone is best prepd. (71–78% yield (74)) from methoxyacetoneitrile with  $\text{C}_6\text{H}_5\text{MgBr}$ ; note also that  $\bar{C}$  with alk. reagents such as  $\text{NaOMe}$  reacts in an unexpectedly complex manner yielding (153) cyclic "halogen-diphenacyls."

$\bar{C}$  with  $\text{NaOEt}$  would be expected to yield  $\omega$ -ethoxyacetophenone [Beil. VIII-90], b.p. 134–136° at 21 mm. (75), 130° at 15 mm. (76), 120–122° at 15 mm. (77),  $D_4^{20} = 1.0552$  (77),  $n_D^{20} = 1.5250$  (77) (corresp. oxime, m.p. 55° (75); corresp. semicarbazone, m.p. 128° (75)); note, however, that no record of this reactn. has been reported and the  $\omega$ -ethoxyacetophenone is best prepd. (68% yield (77)) cf. (75) (76) from ethoxyacetoneitrile with

$C_6H_5MgBr$ ; note also that  $\bar{C}$  with alk. reagents such as  $NaOEt$  reacts in an unexpectedly complex manner yielding (153) cyclic "halogen diphenaclys."

$\bar{C}$  (1 mole) with ethylene glycol (1:6465) (1 mole) in  $C_6H_6$  contg. trace of benzenesulfonic acid gives on hgt. (95% yield (81)) the corresp. cyclic ketal, viz., 2-(chloromethyl)-2-phenyl-1,3-dioxolane, m.p.  $67^\circ$ , b.p.  $144-146^\circ$  at 15 mm. (81).]

With phenols.  $\bar{C}$  with dry sodium phenolate (78) gives  $\omega$ -phenoxyacetophenone [Beil. VIII-91], m.p.  $74^\circ$  cor. (79), b.p.  $255-257^\circ$  (78),  $187^\circ$  cor. at 9 mm. (79) (corresp. semicarbazone, m.p.  $187.0-187.5^\circ$  cor. (70)); note, however, that this prod. is best prepd. (45% yield (79)) from phenoxyacetonitrile with  $C_6H_5MgBr$ , or from phenoxyacetyl chloride +  $C_6H_6$  +  $AlCl_3$  cf. (80).]

With mercaptans.  $\bar{C}$  with  $n$ -BuSH in alc.  $NaOH$  gives (82) phenacyl  $n$ -butyl sulfide, b.p.  $140^\circ$  at 3 mm.,  $D_{25}^{25} = 1.0589$ ,  $n_D^{20} = 1.5050$ .]

$\bar{C}$  with sodium  $p$ -nitrothiophenate in aq. alc. on hgt. gives (98% yield (83)) phenacyl  $p$ -nitrophenyl sulfide, yel. pl. from 50-80%  $AcOH$ , m.p.  $118^\circ$ . —  $\bar{C}$  (1 mole) with sodium  $p$ -thiocresolate (1 mole) in  $MeOH$  boiled several hrs. does not give the expected phenacyl  $p$ -tolyl sulfide, m.p.  $37^\circ$  cf. (101); distillation of the reaction prod. gives (58.5% yield (84)) phenacyl  $p$ -tolyl sulfoxide, b.p.  $182-184^\circ$  at 5 mm., m.p.  $46^\circ$  accompanied by acetophenone; note that with  $H_2O_2$  this sulfoxide oxidizes to phenacyl  $p$ -tolyl sulfone, m.p.  $110^\circ$  (see also below).]

### Behavior with Carbonyl Compounds

With aromatic aldehydes.  $\bar{C}$  (1 mole) with benzaldehyde ( $1\frac{1}{2}$  moles) in alc. with alc.  $NaOEt$  (1 mole) in cold condenses with loss of  $HCl$  giving (80% yield (85))  $\alpha$ -benzoyl- $\alpha'$ -phenyl-ethylene oxide (benzalacetophenone oxide) [Beil. XVII-1-(196)], colorless cryst. from alc. (85) or from cold acetone by addn. of pet. ether (86), m.p.  $89-90^\circ$  (85) (86); note that this prod. can also be obtd. in other ways, notably from benzalacetophenone (chalcone) (1:5155) with  $Na_2O_2$  +  $HCl$  in cold (85% yield (86)) or with  $H_2O_2$  in alc. soln. (90% yield (88)) (87) (89); although *cis* and *trans* stereoisomers are possible, only one form is known.]

$\bar{C}$  with *o*-nitrobenzaldehyde in alc.  $NaOEt$  (although this particular pair has not actually been reported) should yield similarly  $\alpha$ -benzoyl- $\alpha'$ -(*o*-nitrophenyl)ethylene oxide [Beil. XVII-1-(197)] since phenacyl bromide behaves (90) in this fashion; note that for this prod. the two expected geom. stereoisomers are both formed, one with m.p.  $175^\circ$ , the other with m.p.  $110^\circ$ .]

$\bar{C}$  with *m*-nitrobenzaldehyde in alc.  $NaOEt$  (although this particular pair has not actually been reported) should give similarly  $\alpha$ -benzoyl- $\alpha'$ -(*m*-nitrophenyl)ethylene oxide [Beil. XVII-1-(197)] since phenacyl bromide behaves in this manner (80% yield (91)); one stereoisomer is known, m.p.  $118^\circ$  (91). — Note, however, that  $\bar{C}$  (1 mole) with *m*-nitrobenzaldehyde (1 mole) in  $AcOH$  satd. with  $HCl$  gas and stood 24 hrs. reacts differently giving (92) *m*-nitrobenzalacetophenone dichloride [Beil. VII-1-(238)], m.p.  $148^\circ$ .]

$\bar{C}$  (1 mole) with *p*-methoxybenzaldehyde (anisaldehyde) (1:0240) (1 mole) in alc.  $NaOEt$  gives (93)  $\alpha$ -benzoyl- $\alpha'$ -(*p*-methoxyphenyl)ethylene oxide, m.p.  $87^\circ$  (93) (89); also obtd. from *p*-methoxybenzalacetophenone (1:9011) with alk.  $H_2O_2$  (89).]

$\bar{C}$  (1 mole) + *o*-nitrobenzalacetophenone (1 mole) in acetone/dioxane with alc.  $NaOEt$  (1 mole) gives in 15 min. but yield not stated (93) 1,2-dibenzoyl-3-(*o*-nitrophenyl)cyclopropane, m.p.  $177^\circ$  (93).]

### Behavior of $\bar{C}$ with Salts of Organic Acids

$\bar{C}$  with salts of organic acids gives in general the corresp. phenacyl esters although when the latter are to be prepd. as means of identification of the acids the more reactive phenacyl

bromide is usually employed; for m.p.'s of the phenacyl esters of various acids of Order I see Vol. I, p. 650.

[ $\bar{C}$  with KCN in dil. alc. on htg. gives (47% yield (94))  $\omega$ -cyanoacetophenone (benzoyl-acetonitrile) [Beil. X-680, X<sub>1</sub>-(322)], m.p. 83° (94), 80-81° (95) (96); this prod. may also be prepd. by other means, e.g., from phenacyl bromide with dil. alc. KCN (60% yield (97)), or from ethyl benzoate with acetonitrile + NaOEt (yields: 60% (96), 56% (95)).]

[ $\bar{C}$  with KSCN in MeOH (98) or EtOH (65) gives  $\omega$ -thiocyanoacetophenone (phenacyl thiocyanate) [Beil. VIII-94], m.p. 74.1-76.6° cor. (98), 74° (99).]

[ $\bar{C}$  with sodium *p*-toluenesulfinate in boilg. alc. gives (100) cf. (101) phenacyl *p*-tolyl sulfone ( $\omega$ -(*p*-toluenesulfonyl)acetophenone), m.p. 110° (100) (see also above for formn. of this prod. from  $\bar{C}$  + sodium thio-*p*-cresolate).]

### Behavior of $\bar{C}$ with RMgX Compounds

[ $\bar{C}$  (1 mole) with EtMgBr (1 mole) in dry ether gives an addn. prod. which after evapn. of ether, htg. at 130-140°, and hydrolysis gives (yield not stated (102)) benzyl ethyl ketone (1-phenylbutanone-2) [Beil. VI-311, VII<sub>1</sub>-(167)], b.p. 222-227° (103), 221-223° (102), 110° at 13 mm. (101) (corresp. semicarbazone, m.p. 156-156.5° cor (103), 150-153° (103), 153° (106),  $\beta$ -form 152°,  $\alpha$ -form 146° (101), 146° (102), corresp. 2,4-dinitrophenylhydrazone, m.p. 140-141° (103)); not rearr. in formn. of this prod. by this method]

[ $\bar{C}$  with *n*-hexyl-1-yl MgBr in dry ether adds normally and on hydrolysis gives (107) the expected 1-chloro-2-phenyl-1-nonyn-3-ol-2]

### Behavior of $\bar{C}$ with Amines

With primary aliphatic amines. [ $\bar{C}$  (1 mole) with MeNH<sub>2</sub> (2.5 moles) in alc. for 5-6 hrs in cold gives (108)  $\omega$ -(methylamino)acetophenone [Beil. XIV-50, XIV<sub>1</sub>-(369)] (corresp. B.HCl (23% yield (108)), m.p. 210° (108)). —  $\bar{C}$  with *n*-BuNH<sub>2</sub> similarly gives (35% yield (108))  $\omega$ -(*n*-butylamino)acetophenone hydrochloride, m.p. 214-215° (108)]

[ $\bar{C}$  with  $\beta$ -aminoethanol (ethanolamine) readily gives (109) *N*-( $\beta$ -hydroxyethyl)phenacyl-amine, m.p. 144° (109).]

With primary aromatic amines. [ $\bar{C}$  with aniline should yield *N*-(phenacyl)aniline [Beil. XIV-51, XIV<sub>1</sub>-(369)], m.p. 98-99° (110) (corresp. oxime, m.p. 105-106° (111); corresp. semicarbazone, m.p. 171° (110)); however, although the rate of this reaction in abs. alc. at 40° (38) and in 90% alc. at 30.5° (16) cf. (112) has been studied, the usual method of prepn. of *N*-(phenacyl)aniline is from phenacyl bromide + aniline — *Pure N*-(phenacyl)aniline, contrary to earlier statements, is remarkably stable and can be exposed to air at room temp. for 18 months or distilled under reduced press. (b.p. 208-210° at 12 mm.) without change (113); for important study of mechanism of conversion of *N*-(phenacyl)aniline to 2-phenylindole see (113) (114).]

[The behavior of  $\bar{C}$  with the three toluidines has not itself been studied but should be similar to that of phenacyl bromide which with *o*-toluidine gives (115) (116) *N*-(phenacyl)-*o*-toluidine [Beil. XIV-52, XIV<sub>1</sub>-(370)], m.p. 91° (116), 89° (115) (corresp. oxime, m.p. 92° (116)); with *m*-toluidine gives *N*-(phenacyl)-*m*-toluidine, m.p. 110° (117); with *p*-toluidine gives *N*-(phenacyl)-*p*-toluidine [Beil. XIV-52, XIV<sub>1</sub>-(370)], m.p. 134° (118), 127° (115) (corresp. oxime in two geom. stereoisomers of m.p. 97° and 92°, resp. (111))]

With secondary aliphatic amines. [ $\bar{C}$  with Me<sub>2</sub>NH should yield  $\omega$ -(dimethylamino)-acetophenone (phenacyl dimethylamine) [Beil. XIV-50], h.p. 126-128° at 18 mm. (119), 122-123° at 14 mm. (120) (corresp. B.HCl, m.p. 174° (120), corresp. B.HBr, m.p. 184-186° (121), corresp. B.KOH, m.p. 150° (119), 143° (122), 141° (123)); note, however,



that this particular combination of reactants has not actually been reported and that the  $\omega$ -(dimethylamino)acetophenone is usually obt'd. from phenacyl bromide with  $\text{Me}_2\text{NH}$  (119) (121), or from dimethylaminoacet-*N,N*-dimethylamide with  $\text{C}_6\text{H}_5\text{MgBr}$  (80% yield (120) (125)).]

[ $\bar{\text{C}}$  (1 mole) with  $\text{Et}_2\text{NH}$  (2 moles) in  $\text{C}_6\text{H}_6$  stood 2 days at room temp. ppts.  $\text{Et}_2\text{NH}\cdot\text{HCl}$  and gives (65% yield (125))  $\omega$ -(diethylamino)acetophenone, b.p. 148–152° at 30 mm. (125),  $n_D^{25} = 1.5180$  (125).]

[ $\bar{\text{C}}$  + *bis*-( $\beta$ -hydroxyethyl)amine (diethanolamine) in  $\text{C}_6\text{H}_6$  on long boilg. gives (109) *N*-phenacyl-*N,N*-bis-( $\beta$ -hydroxyethyl)amine, m.p. 44° (109).]

With secondary heterocyclic amines. [ $\bar{\text{C}}$  with piperidine in dry ether splits out  $\text{HCl}$  and yields (126)  $\omega$ -(piperidino)acetophenone (*N*-(phenacyl)piperidine) [Beil. XX-42], b.p. 180–181° cor. at 26 mm. (127), 157° at 15 mm. (128), 163–164° at 13 mm. (126),  $D_4^{21.2} = 1.0430$  (126),  $n_D^{22.4} = 1.5403$  (126) (corresp.  $\bar{\text{B}}\cdot\text{HCl}$ , m.p. 226–227° (129), corresp.  $\bar{\text{B}}\cdot\text{HBr}$ , m.p. 227–228° (135), corresp. oxime, m.p. 112–115° (130)).]

[ $\bar{\text{C}}$  with morpholine in dry ether ppts. morpholine  $\text{HCl}$  and yields (131)  $\omega$ -(morpholino)acetophenone (*N*-(phenacyl)morpholine), m.p. 50–52° (132) (corresp.  $\bar{\text{B}}\cdot\text{HCl}$ , m.p. 222–223° cor. (133), 219–223° (134), 213–214° dec. (131), 212–214° (132); corresp.  $\bar{\text{B}}\cdot\text{KOH}$ , m.p. 156–157° (132)).]

[ $\bar{\text{C}}$  (1 mole) with *N'*-phenylpiperazine (2 moles) in dry ether at room temp. for several hrs. (136) or  $\bar{\text{C}}$  (1 mole) with *N'*-phenylpiperazine (1 mole) + slight excess anhydr.  $\text{Na}_2\text{CO}_3$  in alc. refluxed  $\frac{1}{2}$  hr. (136) gives 80–85% yield *N*-phenacyl-*N'*-phenylpiperazine, m.p. 106–108° cor. (136) (corresp.  $\bar{\text{B}}\cdot\text{HCl}$ , m.p. 210–212° cor.; corresp. oxime, m.p. 157–158° cor. (136)).]

[Note, however, that  $\bar{\text{C}}$  with 3-carbethoxy-2-methylpyrrole +  $\text{AlCl}_3$  in  $\text{CS}_2$  does not acylate the nitrogen but gives Friedel-Crafts type reaction yielding (137) 3-carbethoxy-2-methyl-6-phenacylpyrrole, m.p. 205°.]

With tertiary aliphatic amines. [Direct addn. of  $\bar{\text{C}}$  to  $\text{Me}_3\text{N}$  appears not to have been reported; the quaternary salt to be expected, viz., phenacyl-trimethyl-ammonium chloride, m.p. 204° dec. (138), 202° (121), has been prep'd. indirectly.]

With tertiary aromatic amines. [The quaternary salt, viz., dimethyl-phenyl-phenacyl-ammonium chloride, to be expected from  $\bar{\text{C}}$  + dimethylaniline is unreported.]

With tertiary heterocyclic amines. (See also below under  $\bar{\text{D}}$ 's.)

[ $\bar{\text{C}}$  (1 mole) with pyridine (1 + moles) in dry  $\text{C}_6\text{H}_6$  on warming gives (25% yield (139)) phenacyl-pyridinium chloride, m.p. 109–110° (139), 113° (140); note that this prod. with aq. 20%  $\text{NaOH}$  at room temp. . . . . h.p. 127° at 12 mm. (141). — For st . . . . . 5.6° (142) or in 90% alc. at 30.5° (16) cf. (112) see indie. refs.]

#### Behavior of $\bar{\text{C}}$ with Arylhydrazines

(See also below under  $\bar{\text{D}}$ 's.) —  $\bar{\text{C}}$  with many arylhydrazines does not yield the corresp. arylhydrazones because the reaction takes a different course.

$\bar{\text{C}}$  (2 g.) with phenylhydrazine (1.4 g.) in warm  $\text{EtOH}$  (20 ml.) contg.  $\text{NaOAc}\cdot 3\text{H}_2\text{O}$  in aq. (10 ml.) ppts. (14) a yellow solid, m.p. 137° dec. (14), regarded as 1,3-diphenyl-(1,2-diazacyclobutene-2). — Similarly,  $\bar{\text{C}}$  with *o*-tolylhydrazine gives (14) 1-(*o*-tolyl)-3-phenyl-(1,2-diazacyclobutene-2), m.p. 147.2° (14);  $\bar{\text{C}}$  with *p*-tolylhydrazine gives (14) 1-(*p*-tolyl)-3-phenyl-(1,2-diazacyclobutene-2), m.p. 159.8° dec. (14);  $\bar{\text{C}}$  with *p*-nitrophenylhydrazine gives (14) 1-(*p*-nitrophenyl)-3-phenyl-(1,2-diazacyclobutene-2), m.p. 173° dec. (14). — [For further discussion of structures of these prods. see also (143).]

*Behavior of  $\bar{C}$  with Other Miscellaneous Nitrogenous Reactants*

$\bar{C}$  with diazomethane in dry ether + MeOH for 12 hrs. gives (88% yield (144)) 3-chloro-2-phenyl-1,2-epoxypropane ( $\alpha$ -chloromethyl- $\alpha$ -phenyl-ethylene oxide), b.p. 135-137° at 17 mm. (144).]

③ Chloromethyl phenyl ketoxime: cryst. from CS<sub>2</sub>, m.p. 88.5-89° (4), 88-89° (17). [From  $\bar{C}$  (1 mole) + hydroxylamine hydrochloride (3 moles) in dil. MeOH stood overnight, prod. pptd. by addn. of aq. (1); note that this oxime on Beckmann rearr. with PCl<sub>5</sub> gives (4)  $\omega$ -chloroacetanilide, m.p. 134.5° (5).]

④ Chloromethyl phenyl ketone 2,4-dinitrophenylhydrazine: orange cryst., m.p. 212° cor. (145). [See above for behavior of  $\bar{C}$  with various other arylhydrazines.]

⑤ Chloromethyl phenyl ketone semicarbazone: m.p. 160° on "Maquenne bloc" (1), 156° (146), 149° (147). [From  $\bar{C}$  (3.1 g.) in alc. (25 ml.) with semicarbazide hydrochloride (2.2 g.) in aq. (12.5 ml.) at 40° on addn. of NaHCO<sub>3</sub> (1.7 g.) in small increments; yield 71% (147); for study of chem. behavior of this prod. see (147).]

— *N*-(Phenacyl)phthalimide ( $\omega$ -phthalimidoacetophenone) [Bell. XXI-479]: m.p. 167° u.c. (148), 166° (149). [This prod. has never been reported from  $\bar{C}$  + K phthalimide but has been prepd. indirectly. However, for its prepn. from phenacyl bromide with K phthalimide see (150).]

— *N*-(Phenacyl)tetrachlorophthalimide ( $\omega$ -(tetrachlorophthalimido)acetophenone): pl. from CHCl<sub>3</sub> on pouring into MeOH, m.p. 258-259° (151). [From  $\bar{C}$  (?) or phenacyl bromide with K tetrachlorophthalimide (151).]

⑥ Condensation prod. from  $\bar{C}$  with *N*-methyl- $\beta$ -(carbohydrazido)pyridinium *p*-toluenesulfonate: cryst. from EtOH/ether 1:1, m.p. 120° cor. (152). [From  $\bar{C}$  + the quat. salt of nicotinic acid hydrazide with methyl *p*-toluenesulfonate (152).]

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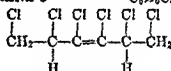
{141} Babcock, Fuson, *J. Am. Chem. Soc.* **55**, 2040-2047 (1933). {142} Allen, Gates, *J. Org. Chem.* **6**, 598-601 (1941). {143} Bodfors, *B. Soc.* 1939, 185. {145} Allen, Fuchs, *Ber.* **41**, 242, Note 1 (1908). {147} Hoogeveen, Gabriel, *Ber.* **41**, 1132 (1908).

{151} Allen, Nicholls, *J. Am. Chem. Soc.* **56**, 1409-1410 (1934). {152} Allen, Gates, *J. Org. Chem.* **6**, 598-601 (1941). {153} Widman, *Ann.* **400**, 86-130 (1913).

### 3:1220 1,2,3,4,5,6-HEXACHLOROHEXENE-3

 $C_6H_2Cl_6$ 

Bell, S.N. 11



M.P. 58-59° (1)

B.P. 110-112° at 2 mm. (1)

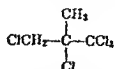
Colorless cryst. from pet ether.

[For prepn from hexadiene-2,5-yne-3 (divinylacetylene) (2) with excess  $\text{Cl}_2$  in  $\text{CCl}_4$  for 12 hrs. (10% yield (1)) see (1)]

$\bar{\text{O}}$  fails to react with  $\text{Cl}_2$  even at elevated temperatures in light, and is unaffected by hot  $\text{HNO}_3$  or by  $\text{O}_3$ ; alk  $\text{KMnO}_4$  causes complete decomposition (1).

3:1220 (1) Coffman, Carothers, *J. Am. Chem. Soc.* **55**, 2040-2047 (1933). (2) Nieuwland, Calcott, Downing, Carter, *J. Am. Chem. Soc.* **53**, 4200-4202 (1931).

### 3:1265 1,1,1,2,3-PENTACHLORO-2-METHYLPROPANE


 $C_4H_2Cl_5$ 

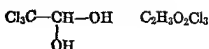
Bell, S.N. 10

M.P. 59.5° (1)

[For prepn. of  $\bar{\text{C}}$  from 1,1,3-trichloro-2-methylpropene-1 (3:5025) with  $\text{Cl}_2$  see (1).]

3:1265 (1) Jacob, *Bull. soc. chim.* (5) **7**, 581-586 (1940).

## 3:1270 CHLORAL HYDRATE



Beil. I - 619  
I<sub>1</sub>-(329)  
I<sub>2</sub>-(680)

M.P. 59-60°	(1) (2)
57°	(3) (4) (5)
54°	(6)
51.6-51.7°	(7)
51.4°	(8)
50.8°	(9)
50.4-50.6°	(10)
50-51°	(11)
48.1°	(17)
47.4°	(6)
46.5-47.5°	(10)
46-47°	(12)
46°	(13)

[See also anhydrous chloral (3:5210) and chloral ethylalcoholate (3:0860).]

The m.p. of  $\bar{C}$  is profoundly affected by mode of heating and by pressure (1) (2) but when taken in test tube in ord. m.p. apparatus is claimed to be consistently 59-60° (2). — [For especially extensive studies on the m.p. of  $\bar{C}$  see (1) (2) (6) (10).]

$\bar{C}$  undergoes a transition point at 32° detectable by dilatometric methods (15). Furthermore,  $\bar{C}$  on heating dissociates into anhydrous chloral and  $\text{H}_2\text{O}$ ; the temperature at which dissocn. begins is unknown, but dissocn. is complete at 78° (15).

Ordinary  $\bar{C}$  is definitely the monohydrate, but other hydrates of chloral (3:5210) have been claimed (6). However, the suggestion (16) that  $\bar{C}$  may exist in two modifications appears to be discredited (6) (10).

[For study of crystal structure of  $\bar{C}$  see (18); for density and refractive index of various solns. of  $\bar{C}$  in aq., EtOH, or toluene see (12); for study of toxicity of  $\bar{C}$  see (10).]

Note that  $\bar{C}$  on hgt. does not give inflammable vapor (diff. from chloral ethylalcoholate (3:0860)).

$\bar{C}$  is eas. sol. in aq. or alc.; much less sol. in  $\text{CHCl}_3$  or toluene. [E.g., 1 pt. aq. dissolves following parts  $\bar{C}$  at indic. temps.: at 0°, 2.4; at 5°, 2.9; at 10°, 3.8; at 15°, 4.9; at 20°, 6.6; at 25°, 8.3; at 30°, 10.1; at 35°, 12.1; at 40°, 14.3 pts.  $\bar{C}$  (20).] — Aq. solns. of  $\bar{C}$  are frequently designated as chloral sirup; for study of stability of such solns. see (21).

CHEMICAL BEHAVIOR OF  $\bar{C}$ 

Important note. The chemistry of chloral hydrate ( $\bar{C}$ ) on one hand and that of anhydrous chloral (3:5210) on the other is so closely interwoven that the division of material between them in this book is necessarily arbitrary. Most of the definite chemical reactions of chloral hydrate have been associated with the text of anhydrous chloral (3:5210), which should always be consulted. Certain methods for the detection and for determination of chloral and chloral hydrate, however, are brought together here under the latter.

DETERMINATION OF  $\bar{C}$ 

For the quantitative detn. of  $\bar{C}$  several different principles have been employed as further explained below.

By behavior with alkali. This method is based upon the fact that  $\bar{C}$  with aq. alkali undergoes hydrolytic cleavage to  $\text{CHCl}_3$  (3:5050) and formic acid (1:1005); since the

latter is neutralized 1 equivalent of alkali is used up for each mole of formic acid produced and therefore for each mole of  $\bar{C}$  originally present. Since on the one hand the  $\text{CHCl}_3$  produced is readily volatile and since on the other it is itself attacked by the excess alkali, some standardization of conditions is required. The process usually involves use of a known amount (excess) of standard alkali followed by back titration with standard acid.

[For especially valuable summaries and discussion of this method see (22) (23); for additional material on characteristics of this method see (24) (25) (26) (27) (28) (29) (30) (31) (32) (33) (34) (35) (41); for discussion of detn. of the formate produced see (22).]

If the sample contains other substances which independently react with alkali and thus interfere with the above method,  $\bar{C}$  may be determined by reduction to acetaldehyde (1:0100) and characterization of the latter. E.g.,  $\bar{C}$  with  $\text{Zn} + \text{strong HCl}$  (36) (37), or with  $\text{Zn} + \text{dil. H}_2\text{SO}_4$  (37) (38) (27) cf. (42), gives acetaldehyde (1:0100); this may be detd. as *p*-nitrophenylhydrazone (36) (or otherwise) or if  $\text{H}_2\text{SO}_4$  was used total chloride ion may be determined (42). This reduction to acetaldehyde is of value in detn. of  $\bar{C}$  in presence of  $\text{CHCl}_3$  (3:5050) or of  $\alpha,\alpha,\beta$ -trichloro-*n*-butyraldehyde ("butyrylchloral") (3:5910) (38).

By determination of total chlorine as chloride ion. In addition to the reduction methods (mentioned in the preceding paragraph) for conversion of all the chlorine of  $\bar{C}$  to chloride ion, this may also be effected by complete hydrolysis with alkali (usually alcoholic alkali best in pressure bottle (39)) (40) (41); for extensive review of methods based on this principle see (22); the total chloride ion is afterward detd. by conventional methods.

By oxidation methods. By appropriate reagents  $\bar{C}$  can be oxidized to trichloroacetic acid (3:1150); by use of a known amount (excess) of standard soln. of oxidant followed by back titration to determine residual oxidant, the amount corresp. to oxidn. of  $\bar{C}$  can be detd. For studies of this method using  $\text{I}_2$  (22) (42) (34) (43),  $\text{Br}_2$  (42),  $\text{KMnO}_4$  (42), or  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (44) see indie. refs.

#### DETECTION OF $\bar{C}$ BY VARIOUS COLOR REACTIONS

With various phenols. [For color tests with resorcinol (1:1530) + aq. alk. (45), with pyrogallol (1:1555) + 60%  $\text{H}_2\text{SO}_4$  (use in distinction from "butyrylchloral" (3:5910) (46)), with phloroglucinol (1:1620) + aq. alkali (47) (49) see indie. refs.]

[For behavior of  $\bar{C}$  with resorcinol (1:1530) +  $\text{KBr} + \text{conc. H}_2\text{SO}_4$  see (52).]

With pyridine + aq. alk. Since  $\bar{C}$  with aq. alk. on warming gives  $\text{CHCl}_3$  (3:5050), detection of the latter by means of the pink to red color produced with pyridine in pres. of conc. aq. alkali (Fujiwara reaction) may be used as indirect test for  $\bar{C}$  (48) (51). Note, however, that the test is not specific since it is given by various other trihalogen compounds. [For further information on the Fujiwara reaction see also under trichloroethylene (3:5170).]

With fuchsin-aldehyde reagent. Note that  $\bar{C}$  (unlike chloral (3:5210)) does not give color with fuchsin-aldehyde reagent (50).

**D 1,1,1-Trichloro-2-methylpropanol-2 ("Chlorethane"):** M.p. 96°. Convert  $\bar{C}$  with aq. alk. to  $\text{CHCl}_3$  (3:5050) and derivatize the latter by combination with acetone to "chloroethane" (3:2662).

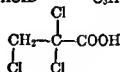
- 3:1270 (1) Bianchetti, *Ann. chim. applicata* **31**, 422-429 (1941), *Chem. Abs.* 1942, 11 1779, C.A. **34**, 2713 (1944). (2) Bianchetti, *Ann. chim. applicata* **31**, 463-466 (1941), *Chem. Abs.* 1942, 11 2577; C.A. **34**, 2714 (1944). (3) Irigoin, *J. Chem. Soc.* 125, 1536-1537 (1924). (4) Meyer, *Dolk. Ann.* 171, 74-76 (1874). (5) Petrikala, *Hochberg. Z. physik. Chem. B-4*, 206 (1929). (6) van Noorden, *Z. physik. Chem.* **67**, 661-712 (1908). (7) Takaloto, *Bull. soc. chim.* (4) **13**, 242-243 (1913). (8) Ballard, *Gaz. chim. ital.* **43**, 1 527 (1913). (9) Hamony, *Yenig. Ind. Trans.* **177**, 1 77 (1885). (10) Woll, *J. Phys. Chem.* **4**, 21-32 (1900). (11) Janczewska, *Ann.* **187**, 243-245 (1871). (12) Rudolph, *Z. physik. Chem.* **37**, 426-447 (1901).

- (13) Personne, *Compt. rend.* 69, 1363 (1869). (14) Berthelot, *Ann. chim.* (5) 12, 536 (1877). (15) Mounfield, Wood, *J. Chem. Soc.* 1926, 498-499. (16) Berthelot, *Ann. chim.* (5) 12, 536 (1877). (17) Kurnakow, Elfremov, *Z. physik. Chem.* 85, 1937; *Cent.* 1938, I 1104; *C.A.* 32, 1998 (1938). *C.A.* 37, 6035 (1943). (20) Speyers, *Am. J. Sci.* (4) 14, 294 (1902). (21) Danckworth, *Arch. Pharm.* 280, 107-205 (1942); *C.A.* 37, 2516 (1943). (22) Watson, *Am. J. Pharm.* 102, 500-525 (1930). (23) Weston, Ellis, *Chem. News* 95, 210-211 (1907). (24) Meyer, Haffter, *Ber. G.* 600-601 (1873). (25) Khait, *Ukrain Gosudarst. Inst. Ekspl. Farm. (Kharkov)* 1939, No. 3, 80-81; *C.A.* 36, 2812 (1942). (26) Goretskii, *Farmatsiya* 1940, No. 6, 31-33; *C.A.* 35, 2678 (1941). (27) Meillere, *J. pharm. chim.* (7) 11, 111-112 (1930). (28) Andron, *J. pharm. chim.* (7) 11, 111-112 (1930). (29) Andron, *Bull. soc. phar.* (1) 1, 111-112 (1927); *C.A.* 21, 2045-2046 (1927). (30) Fleury, Maimy, *J. pharm. chim.* (8) 8, 537-542 (1928); *Cent.* 1929, I 2092; *C.A.* 23, 3775 (1929). (31) Garnier, *Bull. sci. pharmazol.* 1928, I 1898; *C.A.* 22, 1652 (1928). (32) Kolthoff, *J.A.* 2, 448 (1908). (33) Kolthoff, *J.A.* 2, 448 (1908). (34) Kolthoff, *J.A.* 2, 448 (1908). (35) Garnier, *Bull. sci. pharmazol.* 1928, I 1898; *C.A.* 22, 1652 (1928). (36) Griebel, Weiss, *Z. Untersuch. Lebensm.* 56, 163 (1928). (37) Personne, *Ann.* 157, 113-115 (1871). (38) Personne, *Ann.* 157, 113-115 (1871). (39) Personne, *Ann.* 157, 113-115 (1871). (40) Lormand, *J. pharm. chim.* Cent. 1928, II 591; not in *C.A.*

- (1903); *Cent.* 1904, I 480-481. (47) Jaworowski, *Z. anal. chem.* 37, 60-61 (1898). (48) Ross, *J. Biol. Chem.* 58, 641-642 (1923/24). (49) Kul'berg, *Fresman, Farm. Zhur.* 13, No. 3, 12-14 (1940); *Ce* 1941, I 1212; *C.A.* 37, 2882 (1942). (50) Kul'berg, *Fresman, Farm. Zhur.* 13, No. 3, 12-14 (1940); *Ce* 1941, I 1212; *C.A.* 37, 2882 (1942). (51) Adt, *J. pharm. chim.* (8) 22, 68-69 (1928); *Cent.* 1928, II 591; not in *C.A.*

3:1275  $\alpha,\alpha,\beta$ -TRICHLOROPROPIONIC ACID

Beil. II —

II<sub>1</sub> —II<sub>2</sub> (228)

M.P. [65-66° (4)]

60° (1)

50-52° (2)

Colorless very hygroscopic cryst.; note that m.p. is rapidly lowered by exposure to moist air (1). — Eas. sol. aq., alc.,  $\text{C}_6\text{H}_6$ ; best crystd. from  $\text{CS}_2$ .

[For prepn. of  $\bar{\text{C}}$  from  $\alpha,\alpha,\beta$ -trichloropropionaldehyde (3:9033) by oxidn. with fung.  $\text{HNO}_3$  (2) (1) or by aq. acid solns. of chlorates + cat. (4) see indic. refs.; from 1,2,2,3-tetrachlorobutene-3 (3:9060) by oxidn. with excess aq.  $\text{KMnO}_4$  see (3).]

$\bar{\text{C}}$  titrates readily as monobasic acid; Neut. Eq., calcd. 177.5; found, 176.6 (2).

[ $\bar{\text{C}}$  in abs. alc. contg. a little  $\text{H}_2\text{SO}_4$ , refluxed 1 hr. gives (2) ethyl 1,1,2-trichloropropionate, b.p. 121° at 55 mm.,  $D_{25}^{25} = 1.36$ ,  $n_D^{25} = 1.458$  (2).]

[For conversion of  $\bar{\text{C}}$  to acid chloride with  $\text{SOCl}_2$  or  $\text{S}_2\text{O}_2 + \text{Cl}_2 + \text{cat.}$  see (5).]

- 3:1275 (1) Muskat, Becker, *J. Am. Chem. Soc.* 52, 817-818 (1930). (2) Berlande, *Bull. soc. chim.* (4) 37, 1392 (1925). (3) Berchet, Carother, *J. Am. Chem. Soc.* 55, 2098 (1933). (4) Plump (to Pennsylvania Salt Mfg. Co.), U.S. 2,370,577, Feb. 27, 1945; *C.A.* 39, 4985 (1945). (5) Lichty (to Wingfoot Corp.), U.S. 2,361,552, Oct. 31, 1944; *C.A.* 39, 2297 (1945).

3:1280	$\alpha,\alpha,\beta$ -TRICHLORO- <i>n</i> -BUTYRIC ACID (“Trichlorocrotonic acid”)	$  \begin{array}{c}  \text{H} \quad \text{Cl} \\    \quad   \\  \text{CH}_2\text{C} \cdot \text{C} \cdot \text{COOH} \\    \quad   \\  \text{Cl} \quad \text{Cl}  \end{array}  $	$\text{C}_4\text{H}_5\text{O}_2\text{Cl}_3$	Beil. II - 280 II <sub>1</sub> -(124) II <sub>2</sub> -(255)
M.P. 60° (1) 57.9° (2)		B.P. 236-238° (3)		

Colorless hygroscopic lfts. or ndla. from pet. ether; deliquesces in moist air to yield an oil sol. in 20-25 pts. aq. (4). [New comml. prod. (1942) in U.S.A.]

[For prepn. (100% yield (5)) from  $\alpha,\alpha,\beta$ -trichloro-*n*-butyraldehyde hydrate (*n*-butyraldehyde hydrate) (3:1905) via actn. of 2 pts. fuming  $\text{HNO}_2$  ( $D = 1.504$ ) at 30° (5) (6) or with aq. acid solns. of chlorates + cat. (8) see indic. refs.; for prepn. from  $\alpha$ -chlorocrotonic acid (3:2760) or  $\alpha$ -chloro-isocrotonic acid (3:1615) by addn. of  $\text{Cl}_2$  see (1).]

With Zn dust and aq. gives excellent yield (5) of  $\alpha$ -chlorocrotonic acid (3:2760), m.p. 99-100° (5).

$\text{NaA}$  on warming (4) or boilg. (3) with aq. dec. into  $\text{CO}_2$  and 1,1-dichloropropene-1 (3:5120), b.p. 78°. —  $\text{PhA}_2$  (7) or  $\text{PhA}_2 \cdot 2\text{H}_2\text{O}$  (3) is insol. cold aq., spar. sol. hot aq., but eas. sol. in alc. or ether.

With  $\text{PCl}_3$  (3) yields  $\alpha,\alpha,\beta$ -trichloro-*n*-butyryl chloride, b.p. 162-166° (3).

— Methyl  $\alpha,\alpha,\beta$ -trichloro-*n*-butyrate: unreported.

— Ethyl  $\alpha,\alpha,\beta$ -trichloro-*n*-butyrate: b.p. 212° (see 3:6380).

—  $\alpha,\alpha,\beta$ -Trichloro-*n*-butyramide: scales from alc., m.p. 96° (3). [From  $\alpha,\alpha,\beta$ -trichloro-*n*-butyryl chloride (above) with conc. aq.  $\text{NH}_4\text{OH}$  (3).]

—  $\alpha,\alpha,\beta$ -Trichloro-*n*-butyranilide: unreported

—  $\alpha,\alpha,\beta$ -Trichloro-*n*-butyr- $\alpha$ -naphthalide: unreported.

3:1280 (1) Kahlbaum, *Ber.* 12, 2337 (1879). (2) Kendall, *J. Am. Chem. Soc.* 36, 1231 (1914). (3) Judson, *Ber.* 3, 785-788 (1870). (4) Valentin, *Ber.* 29, 2661-2663 (1895). (5) Roberts, *J. Chem. Soc.* 1933, 779. (6) Krämer, Pinner, *Ber.* 3, 349 (1870). (7) Garzaroli-Thurnlack, *Ann.* 182, 184 (1876). (8) Plump (to Pennsylvania Salt Mfg. Co.), U.S. 2,370,577, Feb. 27, 1915; C.A. 39, 4085 (1915).

### 3:1285 2-CHLORONAPHTHALENE


 $\text{C}_{10}\text{H}_7\text{Cl}$ 

Beil. V - 511

 $V_F(202)$ 
 $V_F(445)$ 

M.P.		B.P.		
61°	(1)	256.5° cor.	(20)	$n_D^{20} = 1.60787$ (12)
60°	(2)	256°	(2)	
56.5-60°	(3)	255.6° cor.	at 762 mm. (10)	$(D_4^{20} = 1.178)$ (12)
58.0-59.8°	(1)	264-266° cor.	at 761 mm. (13)	$(n_D^{20} = 1.631)$ (12)
59°	(5)	251-252°	(18)	
58.0°	(6)	121-122°	at 12 mm. (12)	
58.5°	(7)	119.6-119.8°	at 11 mm. (4)	
58-59°	(8)			
58°	(9)			
57.4-57.8°	(10)			
56.7°	(11)			
56.5°	(18)			
56°	(12) (13) (14) (21) (27)			
55°	(15)			

[For 1-chloronaphthalene see 3:6574]



Colorless lfts. from alc.; *cas.* sol. alc., ether,  $C_6H_6$ ,  $CHCl_3$ ,  $CS_2$ . — Volatile with steam.

[For prepn. from  $\beta$ -naphthylamine [Beil. XII-1205, XIII-(532)] via diazotization and use of  $Cu_2Cl_2$  reaction (yields: 00-95% (17), 82% (15), 75-80% (16)) (3) or even on boilg. diazonium salt soln. with conc.  $HCl$  (1) (18), or from diazonium/ $ZnCl_2$  cpd. on addn. to phenol at 60° (44%  $\bar{C}$  + 35% hydroxybiphenyl + 13% diphenyl ether (39)), *see indic. refs.*; from  $\beta$ -naphthol (1:1540) with  $PCl_5$  at 135-140° for 24 hrs. as directed (30% yield (10)) (20) (13) *cf.* (10) or from *tris*-( $\beta$ -naphthyl)phosphoric acid dichloride by hgt. at 310° (21) or from sodium  $\beta$ -naphtholate with  $PCl_5$  in toluene (55% yield (22)) *see indic. refs.*; from sodium  $\beta$ -naphthalenesulfonate with  $PCl_5$  via conv. to  $\beta$ -naphthalenesulfonyl chloride and distn. of latter with a second mole of  $PCl_5$  *see* (13); from mercury *bis*-( $\beta$ -naphthyl) with  $SOCl_2$  *see* (2); from di- $\beta$ -naphthyl sulfone with  $PCl_5$  *see* (23); from 6-chloronaphthoic acid-1 (3:4845) by decarboxylation in quinoline at 225° in pres. of copper chromite cat. *see* (8); for formn. of  $\bar{C}$  in small proportion from 1-chloronaphthalene (3:6878) by hgt. with  $AlCl_3$  (9) or from naphthalene dichloride by actn. of alkali (24) *see indic. refs.*]

[For sepn. of  $\bar{C}$  from 1-chloronaphthalene (3:6878) by fractional freezing of appropriate solutions *see* (25).]

[For thermal anal. of systems of  $\bar{C}$  with  $SbCl_3$  (14) (26) or  $SbBr_3$  (14) *see indic. refs.*; with  $\beta$ -naphthol (1:1540), with  $\beta$ -naphthylamine, or with 2-methylnaphthalene (1:7605) *see* (5), with  $PkOH$  *see* (11).]

[ $\bar{C}$  with even twice calcd. amt. 5%  $Na/Hg$  in alc. for 22 hrs. is *not* reduced but can be recovered almost quant. (27).]

[ $\bar{C}$  with  $Li$  in dry ether subsequently treated with  $MgSO_4$  gives (43% yield (28)) 2-methylnaphthalene (1:7005). —  $\bar{C}$  with chlorobenzene +  $Na$  in xylene refluxed 12 hrs. gives small yield (38) 2-phenylnaphthalene [Beil. V-687, m.p. 101.5° (38).]

[ $\bar{C}$  with strong alc.  $KOH$  in *s.t.* at 220° is unchanged (13), but  $\bar{C}$  with 5 moles 3-25% aq.  $NaOH$  htd. under press. 1 hr. at 350-300° in pres. of  $Cu$  gives (29) a mixt. of  $\beta$ -naphthol (1:1540) +  $\alpha$ -naphthol (1:1500) *cf.* (30).]

[ $\bar{C}$  on mononitration as directed (31) gives 2-chloro-8-nitronaphthalene [Beil. V-556], yel. ndls. from alc., m.p. 116° (31) (of the other theoretically possible mononitro  $\bar{C}$  isomers only the following are known, and these have been prepd. indirectly: viz., 1-nitro-2-chloronaphthalene, m.p. 99-100° (32), 3-nitro-2-chloronaphthalene, m.p. 105° (33), 4-nitro-2-chloronaphthalene, m.p. 79° (34), 6-nitro-2-chloronaphthalene, m.p. 100.5° (37).]

[ $\bar{C}$  on trinitration, e.g., by soln. in 8 pts. nbs.  $HNO_3$  at 0°, nr better (38% yield (15)) by addn. of  $\bar{C}$  (2 g.) to a mixt. of abs.  $HNO_3$  (16 ml.) + conc.  $H_2SO_4$  (8 ml.) at 0°, followed by warming as directed, gives 2-chloro-1,6,8-trinitronaphthalene, pale yel. cryst. from  $AcOH$ , m.p. 193°, white ndls. from  $C_6H_6$ , m.p. 194° (15).]

[ $\bar{C}$  on cat. oxidn. with *nir* at 250-300° gives (35) 53% phthalic anhydride (1:0725) + 47% 4-chlorophthalic anhydride (3:2725).]

[For chloromethylation of  $\bar{C}$  with paraformaldehyde +  $HCl$  gas in  $AcOH$  *see* (40).]

② 2-Chloronaphthalenesulfonamide-8 (7-chloronaphthalenesulfonamide-1): *cryst.* from dil. alc., m.p. 231-232° u.c. (30). [From  $\bar{C}$  with chlorosulfonic acid as directed, followed by conversion of the intermediate 2-chloronaphthalenesulfonyl chloride-8, m.p. 124-126° u.c., with  $(NH_4)_2CO_3$  to desired sulfonamide (30).]

— 2-Chloronaphthalene picrate: m.p. 81.5° (by thermal anal. (11)).

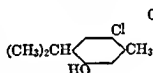
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3:1293 *p*-CHLOROTHYMOL  
(4-Chloro-2-isopropyl-  
5-methylphenol)



$\text{C}_{10}\text{H}_{13}\text{OCl}$

Beil. VI - 539

VI<sub>1</sub>-(266)

VI<sub>2</sub>-(499)

M.P. 62-64° (1) (2) (3)	B.P. 259-263° (10)
61° (4)	258-259° (3)
59-60° (5) (6)	143-147° at 18-20 mm. (4)
59° (7)	
58° (8)	
58-60° (9)	

[See also *p*-chlorocarracrol (3:0480)]

Note that  $\bar{C}$  is also known as 4-chlorothymol (Beilstein) and as 6-chlorothymol (C.A.) according to differing methods of numbering the thymol nucleus.

### PREPARATION OF $\bar{C}$

From thymol. [For prepn. of  $\bar{C}$  from thymol (1:1430) by chlorination with  $\text{Cl}_2$  in aq.  $\text{Na}_2\text{CO}_3$  (80% yield (10)), with  $\text{Cl}_2$  in  $\text{AcOH}$  (50% yield (8)), or with  $\text{SO}_2\text{Cl}_2$  (1) (9) in  $\text{CHCl}_3$  (5) see indic. refs.]

From 4-chloro-3-methylphenol (4-chloro-*m*-cresol). [For prepn. of  $\bar{C}$  from 4-chloro-3-methylphenol (3:1535) by conversion with isopropyl alcohol or isopropyl chloride

(3:7025) (11) or with propylene (3) to 4-chloro-3-methylphenyl isopropyl ether and subsequent rearr. (11) (3), e.g., with  $\text{H}_2\text{SO}_4/\text{AcOH}$  (6), to  $\bar{\text{C}}$ , see indic. refs.]

From other sources. [For prepn. of  $\bar{\text{C}}$  from 4-amino-2-isopropyl-5-methylphenol via diazotization and use of  $\text{CuCl}_2/\text{ZnSO}_4$  see (4).]

### BIOCHEMICAL ASPECTS AND USES OF $\bar{\text{C}}$

$\bar{\text{C}}$  as a halogenated phenol has been widely considered as an antiseptic, bactericide, disinfectant, germicide, fungicide, etc.; while this aspect cannot here be recorded in detail, the following examples may serve as leading references.

[For general and technical articles on bactericidal (12) (13) (14) (15) (16) (17) (18), fungicidal (12) (19) (20) (21), or anthelmintic (22) action of  $\bar{\text{C}}$  see indic. refs.; for patents on various means of improving the aqueous solubility of  $\bar{\text{C}}$  for use as germicide see (23) (24) (25) (26) (27) (28) (2) (29); for patent on use of  $\bar{\text{C}}$  in mouthwash see (30); for use as disinfectant of a mixt. of  $\bar{\text{C}}$  (2 pt.) with camphor (1 pt.) (which mixt. is liquid above  $5^\circ$ ) see (31).]

### CHEMICAL BEHAVIOR OF $\bar{\text{C}}$

Reduction. [ $\bar{\text{C}}$  in aq. alk. with  $\text{H}_2$  + cat. at  $180^\circ$  and 30 atm. (32), or  $\bar{\text{C}}$  in aq. alk. with Fe filings at  $170^\circ$  or at  $200^\circ$  under pressure (33) gives (100% yield (32)) thymol (1:1430), m.p.  $51.5^\circ$ .]

Oxidation.  $\bar{\text{C}}$  on oxidation with  $\text{CrO}_3$  (8) or with  $\text{MnO}_2$  in ice-cold conc.  $\text{H}_2\text{SO}_4$  (1) gives thymoquinone (1:9003), m.p.  $45.5^\circ$ .

### Reactions Involving Nuclear Substitution of $\bar{\text{C}}$

Bromination. [ $\bar{\text{C}}$  with  $\text{Br}_2$  in  $\text{AcOH}$  gives (8) a mixt. of products.]

Nitration. [ $\bar{\text{C}}$  in lt. pct. floated on an aqueous soln. of nitrous acid (from  $\text{NaNO}_2 + \text{HCl}$ ) for a week gave (8) 4-chloro-2-isopropyl-5-methyl-6-nitrophenol [Beil. VI-542, VI-1-(267)], pale yel. ndls. from alc., m.p.  $116^\circ$  (8) (34). — Note that attempts to effect direct nitration of  $\bar{\text{C}}$  with  $\text{HNO}_3$  in  $\text{AcOH}$  below  $20^\circ$  (8) give a mixt. of products; also that  $\bar{\text{C}}$  in dry  $\text{CHCl}_3$  at  $-20^\circ$  with  $\text{NO}_2$  (from btg. dry  $\text{Pb}(\text{NO}_3)_2$ ) gives (8) 4-chloro-3,4,6-trinitro-2-isopropyl-5-methyl-cyclohexadien-2,5-dione-1 [Beil. VII-1-(100)], yel. cryst., m.p. about  $105^\circ$  dec. (8).]

Mercuration. [For patents on mercuration of  $\bar{\text{C}}$  see (35) (36).]

Miscellaneous nuclear substitutions. [Note that  $\text{Na}\bar{\text{A}}$  with benzyl chloride (3:8535) in toluene at  $110^\circ$  for 4 hrs. gives (by nuclear benzylation) (37) 4-chloro-6-benzyl-2-isopropyl-3-methylphenol, b.p.  $180^\circ$  at 3 mm. (37).]

[ $\bar{\text{C}}$  with  $\text{SCl}_2$  in  $\text{CS}_2$  gives (65% yield (5)) a sulfide,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{Cl}_2\text{S}$ , m.p.  $110-111^\circ$ , of undetermined structure.]

### Reactions Involving the Phenolic Group of $\bar{\text{C}}$

(See also below under  $\bar{\text{C}}$ 's.)

[ $\bar{\text{C}}$  with  $\text{PCl}_5$  at  $180-200^\circ$  for 2 hrs. gives (9) 2,5-dichloro-p-cymene [Beil. V-423, V-2-(326)], h.p.  $240-243^\circ$ ; this prod. on oxidn. with dil.  $\text{HNO}_3$  ( $D = 1.15$ ) in s.t. at  $180^\circ$  for 10 hrs. gives (38) 2,5-dichloroterephthalic acid [Beil. IX-847], m.p.  $305^\circ$  (38) (corresp. dimethyl ester, m.p.  $136^\circ$  (38)).]

[For behavior of  $\bar{\text{C}}$  with  $\text{POCl}_3$  giving compds. of types  $\text{ROPOCl}_2$  and  $(\text{RO})_2\text{POCl}$  ( $\text{R} = p\text{-chlorothymyl}$ ) see (39); for clinical tests of sodium salt of  $p\text{-chlorothymylphosphoric}$  acid "thymophogen") with tuberculosis see (40); for prepn. of such salt see (41).]

—  $p\text{-Chlorothymyl}$  methyl ether: oil, b.p.  $251^\circ$  cor. at 760 mm. (1). [From  $\bar{\text{C}}$  with  $\text{MeI} + \text{KOH}$  (1) or from thymyl methyl ether with  $\text{SO}_2\text{Cl}_2$  (42).]

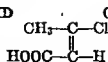
- *p*-Chlorothymyl ethyl ether: unreported.  
 — *p*-Chlorothymyl acetate: oil, b p. 112–114° at 2 mm. (43). [From  $\bar{C}$  with  $Ac_2O$  (9) or  $AcCl$  (44); for Fries rearr. to the corresp. acetophenone deriv. see (44) cf. (43).]  
 (9) *p*-Chlorothymyl benzoate: m.p. 71–73° (9). [From  $\bar{C}$  with  $BzCl$  in aq.  $KOH$  (9).]  
 (7) *p*-Chlorothymyl benzyl ether: m.p. 55° (7).  
 (7) *p*-Chlorothymyl *o*-nitrobenzyl ether: m.p. 117° (7).  
 — *p*-Chlorothymyl *p*-nitrobenzyl ether: unreported.  
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3:1300  $\beta$ -CHLOROISOCROTONIC ACID

(cis-3-Chlorobuten-2-oic acid-1)

 $\text{C}_4\text{H}_5\text{O}_2\text{Cl}$  · Beil. II - 416 $\Pi_1$ -(190) $\Pi_2$ -(396)

M.P. 62°	(1)	B.P. 104.8° cor. (11)	$D_4^{25} = 1.1995$ (7)
61.5°	(2)		$n_D^{25} = 1.47039$ (7)
61°	(3) (4) (5)		
	(6) (7) (8)		
60.5°	(9)		
50.5-60.5°	(10)		
59.5°	(11) (17)		

[See also  $\beta$ -chlorocrotonic acid (3:2625).]

Cryst. from aq. or pet. ether. —  $\bar{C}$  is somewhat less sol. in aq. than its stereoisomer (3:2625); e.g.,  $\bar{C}$  is sol. in 52.4 pts. aq. at 19° (12), in 79 pts. aq. at 7° (11). —  $\bar{C}$  is very easily volatile with steam (11) (dif. from  $\beta$ -chlorocrotonic acid (3:2625)). —  $\bar{C}$  in either *cis*- $\alpha,\beta$ -dichloroethylene (3:5042) or *trans*- $\alpha,\beta$ -dichloroethylene (3:5028) is very much more sol. than the stereoisomeric  $\beta$ -chlorocrotonic acid (3:2625) (13). —  $\bar{C}$  sublimes even at room temp. (11).

For f.p./compn. data and diagram of system  $\bar{C}$  + the stereoisomeric  $\beta$ -chlorocrotonic acid (3:2625) (eutectic, m.p. 38.9° contg. 66.8 molo %  $\bar{C}$ ) see (14).

Preparation. [The most frequently used method of prepn. of  $\bar{C}$  is that from ethyl acetoneacetate (1:1710) with  $\text{PCl}_5$ ; this treatment leads to the formn. of a mixt. of the acid chlorides of  $\bar{C}$  and the stereoisomeric  $\beta$ -chlorocrotonic acid (3:2625) which upon hydrolysis with aq. gives a mixt. of the two acids; from this mixture  $\bar{C}$  is removed (together with any unreacted ethyl acetoneacetate) by distillation with steam; the yield of mixed acids is variously reported, e.g., 43.7% (3), 36.5% (9); the yield of  $\bar{C}$  is relatively small, e.g., 26.8% (3), 13% (1). — The  $\text{PCl}_5$  reactn. has often been carried out in dry  $\text{C}_6\text{H}_6$  (8) (15) (9) (3), but its use is regarded (1) as disadvantageous. — For many important details of procedure see indic. refs.]

[For formn. of  $\bar{C}$  from  $\alpha,\beta,\beta$ -trichloro-*n*-butyric acid (3:0925) by removal of the  $\alpha$ - and one  $\beta$ -chlorine atom with Zn see (16); from the stereoisomeric  $\beta$ -chlorocrotonic acid (3:2625) by hgt. at 150-160° for 20 hrs. (17) or at 130° in s.t. (18) see indic. refs.]

Chemical behavior. [ $\bar{C}$  in alc. or in aq. NaOH with  $\text{H}_2$  + Pd/BaSO<sub>4</sub> (4), or  $\bar{C}$  (as Na $\bar{A}$ ) with 2½% Na/Hg in aq. (19), yields mainly isocrotonic acid (1:1045) together with some crotonic acid (1:0425) and tetrolic acid,  $\text{CH}_3-\text{C}\equiv\text{C}-\text{COOH}$ ; note that  $\bar{C}$  is thus dehalogenated more rapidly (4) than the stereoisomeric  $\beta$ -chlorocrotonic acid (3:2625), and that with excess  $\text{H}_2$  the products are further reduced to *n*-butyric acid (1:1035).]

$\bar{C}$  on oxidn. with aq.  $\text{KMnO}_4$  yields (20) only AcOH (1:1010) and oxalic acid (1:0445).

$\bar{C}$  with  $\text{Cl}_2$  in  $\text{CS}_2$  soln. adds 1 mole halogen yielding (16)  $\alpha,\beta,\beta$ -trichloro-*n*-butyric acid (3:0925), m.p. 52°;  $\bar{C}$  undoubtedly adds 1  $\text{Br}_2$  to yield  $\beta$ -chloro- $\alpha,\beta$ -dibromo-*n*-butyric acid but the latter has never been reported.

$\bar{C}$  behaves as a monobasic acid; dissociation const. at 25° =  $9.47 \times 10^{-5}$  (21). —  $\bar{C}$  on neutralization with cold dil. alk. gives Neut. Eq. 120.5. — Note, however, that with strong aq. KOH  $\bar{C}$  is somewhat more resistant than its stereoisomer (3:2625); e.g.,  $\bar{C}$  with 3-4 *N* KOH at 115-120° (16) cf. (22) gives acetone (1:5400) +  $\text{K}_2\text{CO}_3$  + KCl; with 7-8% KOH at 125-130° same + some tetrolic acid.

Salts. [ $\text{NH}_4\text{H}\bar{A} \cdot \text{H}_2\text{O}$  (11);  $\text{Na}\bar{A} \cdot \frac{1}{2}\text{H}_2\text{O}$ , very sol. aq. or slc. (11);  $\text{K}\bar{A} \cdot \text{H}_2\text{O}$ , sol. in 13.2 pts. alc. at 14° (24);  $\text{Ag}\bar{A}$ , alm. insol. cold aq.; on hgt. with aq. in s.t. at 170° dec. much more readily (24) than its stereoisomer (3:2625) into  $\text{CO}_2$  + propadiene (allylene):

$\text{Mg}\bar{\text{A}}_2 \cdot 5\text{H}_2\text{O}$ ,  $\text{Ca}\bar{\text{A}}_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ba}\bar{\text{A}}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Zn}\bar{\text{A}}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ,  $\text{Mn}\bar{\text{A}}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Co}\bar{\text{A}}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}\bar{\text{A}}_2 \cdot 6\text{H}_2\text{O}$ , all sol. aq. (11);  $\text{Pb}\bar{\text{A}}_2 \cdot 4\text{H}_2\text{O}$ , spar. sol. aq. (11).]

$\bar{\text{C}}$  with  $\text{PCl}_5$  (25) or with  $\text{SOCl}_2$  (26) gives (yield 90% (26)) (29)  $\beta$ -chloroisocrotonyl chloride, b.p.  $135\text{--}136^\circ$  at 760 mm.; see also comments under  $\beta$ -chlorocrotonic acid (3:2625).

[ $\bar{\text{C}}$  (as  $\text{K}\bar{\text{A}}$ ) with alc.  $\text{NaOEt}$  on bfg. gives after acidification (17)  $\beta$ -ethoxycrotonic acid [Beil. III-371, III<sub>1</sub>-(135)], m.p.  $137\text{--}138^\circ$  (17),  $141^\circ$  (27); note that during reactn. isomerization has occurred and that this prod. is the same as is similarly obtd. from  $\beta$ -chlorocrotonic acid (3:2625). —  $\bar{\text{C}}$  (as  $\text{Na}\bar{\text{A}}$ ) with  $\text{Na}$  benzylate on bfg. gives after acidification (28)  $\beta$ -benzyloxycrotonic acid, m.p.  $121\text{--}122^\circ$  (28), the same as does the stereoisomer. —  $\bar{\text{C}}$  (as  $\text{Na}\bar{\text{A}}$ ) with  $\text{Na}$  salt of benzyl mercaptan in alc. on hfg. gives after acidification (28)  $\beta$ -benzylmercaptoisocrotonic acid, m.p.  $130^\circ$ ; note that here isomerization does not occur.]

[For behavior of  $\bar{\text{C}}$  (as  $\text{NH}_4\bar{\text{A}}$ ) with  $(\text{NH}_4)_2\text{SO}_3$  yielding  $\beta$ -sulfoisocrotonic acid (3), or of  $\bar{\text{C}}$  (as  $\text{K}\bar{\text{A}}$ ) with  $\text{K}_2\text{AsO}_3$  yielding (10)  $\beta$ -arsonocrotonic acid, see indic. refs.; note that in both cases the products are identical with those obtd. by similar treatment of  $\beta$ -chlorocrotonic acid (3:2625)]

— Methyl  $\beta$ -chloroisocrotonate: b.p.  $142^\circ$ . See 3:8028. [For rate of esterification of  $\bar{\text{C}}$  with  $\text{MeOH}$  see (30).]

— Ethyl  $\beta$ -chloroisocrotonate: b.p.  $165^\circ$ . See 3:8325.

②  $\beta$ -Chloroisocrotonamide: lfts. from aq., m.p.  $109\text{--}110^\circ$  (25). [From  $\beta$ -chloroisocrotonyl chloride (see above) with conc. aq.  $\text{NH}_4\text{OH}$  (25).] [For study of solubility in *cis*-1,2-dichloroethylene (3:5042) and in *trans*-1,2-dichloroethylene (3:5028) see (13).]

③  $\beta$ -Chloroisocrotonanilide: ndls. from alc., m.p.  $106^\circ$  (25). [From  $\beta$ -chloroisocrotonyl chloride (see above) with aniline + excess cold dil. aq.  $\text{NaOH}$  in 100% yield (25).]

④  $\beta$ -Chloroisocroton- $\alpha$ -naphthalide: ndls. from alc., m.p.  $155^\circ$  (25). [From  $\beta$ -chloroisocrotonyl chloride (see above) with  $\alpha$ -naphthylamine + excess cold dil. aq.  $\text{NaOH}$  in 100% yield (25).]

3:1300 (1) Dadiou, Pongrutz, Kohlrausch, *Monatsh.* 60, 211-212 (1932); *Sitzber. Akad. Wiss. Wien, Math. naturw. Klasse, Abt. II-a.* 140, 359-360 (1931). (2) Stelling, *Z. physik. Chem.* B-24, 423 (1934). (3) Backer, Beute, *Rec. trav. chim.* 54, 552-553, 559-560 (1933). (4) Paal, Schiedewitz, Rauscher, *Ber.* 64, 1521-1530 (1931). (5) Bruylants, Castille, *Bull. soc. chim. Belg.* 34, 277 (1925). (6) von Auwers, Wissebach, *Ber.* 56, 724 (1923). (7) von Auwers, *Ber.* 45, 2807 (1912). (8) Michael, Schulthess, *J. prakt. Chem.* (2) 46, 236-237 (1892). (9) Skau, Saxton, *J. Am. Chem. Soc.* 50, 2693-2701 (1928). (10) Backer, van Oosten, *Rec. trav. chim.* 59, 59 (1940).

(11) Geuther, Fröhch, *Zeit. Chem.* 1869, 270-271. (12) Michael, Brown, *Am. Chem. J.* 9, 284 (1887). (13) Lebrun, *Bull. soc. chim.* 39, 429-430 (1930). (14) Skau, Saxton, *J. phys. Chem.* 37, 183-186 (1933). (15) Scheibler, Voss, *Ber.* 53, 381-382 (1920). (16) Szeic, Taggesell, *Ber.* 28, 2665-2667 (1895). (17) Friederich, *Ann.* 219, 327-316, 363 (1883). (18) Michael, Schulthess, *J. prakt. Chem.* (2) 46, 264-266 (1892). (19) Michael, Schulthess, *J. prakt. Chem.* (2) 46, 250-251 (1892). (20) Kondakow, *J. Russ. Phys.-Chem. Soc.* 24, 511 (1892).

(21) Ostwald, *Z. physik. Chem.* 3, 245 (1889). (22) Michael, *J. prakt. Chem.* (2) 38, 9-10 (1888). (23) Michael, Schulthess, *J. prakt. Chem.* (2) 46, 254-255 (1892). (24) Michael, Clark, *J. prakt. Chem.* (2) 52, 326-329 (1895). (25) Autenrieth, *Ber.* 29, 1665-1670 (1896). (26) Scheibler, Topouzada, Schulze, *J. prakt. Chem.* (2) 124, 16 (1930). (27) Nef, *Ann.* 276, 234 (1893). (28) Autenrieth, *Ber.* 29, 1646-1648 (1896). (29) Scheibler, Voss, *Ber.* 53, 382 (1920). (30) Sudborough, Roberts, *J. Chem. Soc.* 87, 1846 (1905).

(31) Michael, Oechslin, *Ber.* 42, 322 (1909).

## 3:1310 1,3-DICHLORONAPHTHALENE

 $C_{10}H_8Cl_2$ 

Beil. V - 542

V<sub>1</sub>-(262)V<sub>2</sub>-(445)

M.P. 61.5-62° (1)

61.5° (2)

61° (3) (6) (12)

B.P. 291° cor. at 775 mm. (4)

Colorless ndls. from alc. — Volatile with steam (4).

[For prepn. of  $\bar{C}$  from 1-amino-2,4-dichloronaphthalene via diazotization and subsequent warming with alc. see (4) (5) (6) (1); similarly from 1-amino-5,7-dichloronaphthalene see (7); from 4-nitronaphthalene-sulfonyl chloride-2 by hgt. with excess  $PCl_5$  see (3) (8); from naphthalene-1,3-bis-(sulfonyl chloride) by distn. with  $PCl_5$  see (2); from naphthalene-tetrachloride-1,2,3,4 (3:4750) with alc. KOH see (9) (10) (4) (11).]

[ $\bar{C}$  in  $CHCl_3$ , satd. with  $Cl_2$  at ord. temp. yields (4) 1,2,4-trichloronaphthalene (3:2490), m.p. 92° (4).]

[ $\bar{C}$  on nitration yields (4) a mixt. of two dinitro cpds., m.p. 150° and 158° respectively.]

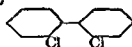
[ $\bar{C}$  in  $CS_2$  treated with  $ClSO_3H$  (12) yields a mixt. of 1,3-dichloronaphthalenesulfonic acid-5 [Beil. XI-163] (corresp. sulfonyl chloride, m.p. 148.5°, corresp. sulfonamide, m.p. 272° (12)) and 1,3-dichloronaphthalenesulfonic acid-7 [Beil. XI-183] (corresp. sulfonyl chloride, m.p. 121°, corresp. sulfonamide, m.p. 228° (12)).]

$\bar{C}$  on oxidn. with  $CrO_3$  in  $AcOH$  yields (4) phthalic acid (1:0820) + 2-chloronaphthoquinone-1,4 (3:3580), m.p. 115° (4). —  $\bar{C}$  on oxidn. in s.t. with conc.  $HNO_3$  yields (5) phthalic acid (1:0820).

3:1310 (1) Weissberger, Sängewald, Hampson, *Trans. Faraday Soc.* 30, 890 (1934). (2) Armstrong, Wynne, *Chem. News* 61, 93 (1890). (3) Cleve, *Ber.* 10, 2181 (1886). (4) Cleve, *Ber.* 23, 954-955 (1890). (5) Cleve, *Ber.* 20, 449 (1887). (6) Erdmann, *Ann.* 215, 260-261 (1893). (7) Erdmann, *Ber.* 21, 3445 (1888). (8) Cleve, *Ber.* 21, 3274 (1888). (9) Faust, *Saame, Ann.* 160, 69 (1871). (10) Widman, *Ber.* 15, 2161-2162 (1882).

(11) Armstrong, Wynne, *Chem. News* 58, 264-265 (1888). (12) Armstrong, Wynne, *Chem. News* 61, 274, 284 (1890).

## 3:1325 2,2'-DICHLOROBIPHENYL

 $C_{12}H_8Cl_2$ 

Beil. V —

V<sub>1</sub>-(272)V<sub>2</sub>-(483)

M.P. 61-62° (11)

60.7-62 (1)

60.5-61° (2)

60.5° (3)

60° (4)

59.0-60.5° (5)

59° (6) (7) (8)

58-59° (10)

Pr. from pet. eth. or  $MeOH$ .

[For prepn. of  $\bar{C}$  from *o*-chloriodobenzene [Beil. V-220, V<sub>1</sub>-(119)] by hgt. with  $Cu$  powder under various conditions (yield: 40% (1), 20% (11), 10% (2)) see indic. refs.; from 2,2'-dinitrobiphenyl [Beil. V-583, V<sub>1</sub>-(273)] with  $SOCl_2$  in s.t. at 200-210° for 10 hrs. see (7); from 2,2'-diaminobiphenyl [Beil. XIII-210, XIII<sub>1</sub>-(57)] via tetrazotization and reaction with  $Cu_2Cl_2$  (6) or by decomp. of  $HgCl_2$  complex (80% yield (3)) see indic. refs.; for dis-

cussion of formn. from chlorobenzene (3:7903) during prepn. of phenol by alk. fusion see (12).]

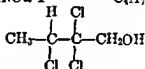
$\bar{C}$  on dinitration with mixt. of conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$  as directed (13) (9) gives (41% yield (13)) 2,2'-dichloro-5,5'-dinitrobiphenyl, cryst. from acetone, m.p. 203-204° (13), 205° (9) (a small amt. of an isomer, m.p. 128-129°, is also formed (13));  $\bar{C}$  on tetranitration by htg. with mixt. of 5 pts. fuming  $\text{HNO}_3$  ( $D = 1.6$ ) + 20 pts. conc.  $\text{H}_2\text{SO}_4$  at 100° for 2 hrs. (13) (4) gives (38% yield (13)) 2,2'-dichloro-3,5,3',5'-tetranitrobiphenyl, cryst. from dioxane, m.p. 307-308° (13) (this prod. after melting is converted to higher-melting form, m.p. 316°, recrystn. of which from alc. restores the lower-melting variety (9)).

3:1325 (1) Hampson, Weissberger, *J. Am. Chem. Soc.* 58, 2117 (1936). (2) Weissberger, Sängewald, *Z. physik. Chem. B-20*, 155 (1933). (3) Schwechten, *Ber.* 65, 1607 (1932). (4) van Alphen, *Rec. trav. chim.* 51, 454-455 (1932). (5) Williamson, Rodebush, *J. Am. Chem. Soc.* 63, 3019 (1941). (6) Dobbie, Fox, Gauge, *J. Chem. Soc.* 99, 1619 (1911). (7) Mascarelli, Gatti, *Gazz. chim. ital.* 59, 868 (1929). (8) Mascarelli, Gatti, *Gazz. chim. ital.* 63, 664 (1933). (9) Mascarelli, Gatti, *Gazz. chim. ital.* 63, 658 (1933). (10) Brüll, *Gazz. chim. ital.* 65, 24 (1935). (11) Bretscher, *Helv. Phys. Acta* 2, 266-267 (1929). (12) Hale, Britton, *Ind. Eng. Chem.* 20, 122 (1923). (13) Case, Schock, *J. Am. Chem. Soc.* 65, 2086-2087 (1943).

### 3:1336 *d,l*-2,2,3-TRICHLOROBUTANOL-1

$\text{C}_4\text{H}_7\text{OCl}_3$

Beil. I - 369



$I_1 -$

$I_2 - (398)$

M.P. 62° (1) (3) (6) B.P. 199-200° (4)  
61.5-62° (2) 120° at 45 mm. (2)  
[57° (8)]

Cryst. from pet. ether. — Insol. cold aq.; spar. sol. bot aq.; eas. sol. alc., ether. — In small quantities can (with caution) be sublimed (2).

[For prepn. of  $\bar{C}$  from  $\alpha,\alpha,\beta$ -trichloro-*n*-butyraldehyde (butyrylchloral) (3:5910) with fused  $\text{Al}(\text{OEt})_3$  in boilg. abs. alc. under  $\text{H}_2$  or  $\text{N}_2$  for 14 hrs. (92% yield (1)), or with fused  $\text{Al}(\text{OEt})_3 + \text{AlCl}_3$  in boilg. abs. alc. under  $\text{H}_2$  or  $\text{N}_2$  for 14 hrs. (3), or with  $\text{C}_2\text{H}_5\text{OMgBr}$  in dry ether followed by aq. (5), or by treatment with diethylzinc (60-70% yield (8)) (2), di-*n*-propylzinc (6), or di-isobutylzinc (6) followed by aq. see indic. refs; for formn. of  $\bar{C}$  from urobutyrylchloral acid (see below) by hydrolysis see (4).] [Note that dextro-rotatory  $\bar{C}$ , m.p. 62°, is obtd. (7) from butyrylchloral hydrate (3:1905) by action of fermenting yeast.]

[ $\bar{C}$  with Zn + very dil. HCl gives (2) 2-chlorobuten-2-ol-1 (3:8240), b.p. 158°. —  $\bar{C}$  reduces Fehling soln. on warming.]

$\bar{C}$  on oxidn. with conc.  $\text{HNO}_3$  gives  $\alpha,\alpha,\beta$ -trichloro-*n*-butyric acid (3:1280).

$\bar{C}$  with  $\text{PCl}_5$  on htg. gives (30-40% yield (8)) (2) 1,2,2,3-tetrachlorobutane (3:9078) (volatile with steam) accompanied by much (non-volatile) *trans*-(2,2,3-trichloro-*n*-butyl)-phosphate, colorless ndls. from alc., m.p. 85.3-85.4° (8).

[ $\bar{C}$  is sol. in conc.  $\text{H}_2\text{SO}_4$  on slight warming but readily decomposes if btg. is excessive (2).  $\bar{C}$  does not react with  $\text{PCl}_5$ , or with fuming  $\text{HBr}$  even at 110° (2).]

$\bar{C}$  on administration to dogs is excreted in the urine as urobutyrylchloral acid [Beil. I-664] (4).

— 2,2,3-Trichloro-*n*-butyl acetate: b.p. 217.5° at 730 mm., 131-132° at 70 mm. (2).

[From  $\bar{C}$  with  $\text{AcCl}$  in a t. at 110° for several hrs. (2).]



3:1336 (1) Meerwein, Schmidt, *Ann.* 444, 233-234 (1925). (2) Garzaroli-Thurnlackh, *Ann.* 213, 369-379 (1882). (3) Meerwein (to F. Bayer and Co.), U.S. 1,572,742, Feb. 9, 1926; *Cent.* 1926, I 3627; *Brit.* 251,680, June 2, 1926; *Cont.* 1926, II 1007. (4) Meier, *Z. phys. Chem.* 100, 496 (1882).

Papper, *Ann.*

I 2301; *C.A.* 20, 2400 (1926). [For structure, *Ann.* 444, 233-234 (1925).]

### 3:1340 2,3,5-TRICHLOROPHENOL


 $C_6H_2OCl_3$ 

Beil. VI —

VI<sub>1</sub>—

VI<sub>2</sub>—(180)

M.P. 63° (1) (2) (3)

$\bar{C}$  when dislvd. in hot solvents and cooled gives gels; e.g., a very dil. hot aq. soln. set on cooling to an almost solid translucent gel, partly fibrous and partly crystalline (1). When a soln. of  $K_2CrO_4$  is poured on such a gel contg.  $AgNO_3$ , distinct but not well-defined Liesegang rings are produced in the gel (1) cf. (4).

$\bar{C}$  is volatile with steam. — Ionization const. at 23° is  $5.0 \times 10^{-8}$  (3);  $\bar{C}$  can be titrated with  $N/10$  alk. using phenolphthalein; Neut. Eq. 197.5 (2).

[For prepn. from 2,3,5-trichloroaniline via diazo reaction see (1) (70% yield) or (2) (57% yield).]

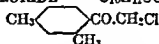
$\bar{C}$  (1.5 g.) dislvd. in 20% aq. NaOH (20 ml.) and shaken with  $(CH_3)_2SO_4$  (5 g.) ppts. (1) methyl ether (1.5 g. = 94% yield), 2,3,5-trichloroanisole, adls. from alc., m.p. 84° (1), cryst. from acetone, m.p. 82° (4).

⊕ 2,3,5-Trichlorophenyl benzoate: from  $\bar{C}$  +  $BzCl$  + aq. NaOH, adls. from alc., m.p. 101° (4), from lgr., m.p. 103° (4).

3:1340 (1) Hodgson, Kershaw, *J. Chem. Soc.* 1929, 2919-2921. (2) Tiessens, *Rec. trav. chim.* 50, 114 (1931). (3) Tiessens, *Rec. trav. chim.* 49, 1066-1068 (1929). (4) Holleman, *Rec. trav. chim.* 39, 739-740 (1920).

### 3:1355 2,4-DIMETHYLPHENACYL CHLORIDE

( $\omega$ -Chloro-2,4-dimethylacetophenone)


 $C_{10}H_{11}OCl$ 

Beil. VII - 324

VII<sub>1</sub>—(172)

M.P. 62°

Long wh. lfts. (from alc.). [For prepn. from *m*-xylene, chloroacetyl chloride (3:5235) +  $AlCl_3$  see (1) (3).]

$\bar{C}$  on oxidn. with aqueous NaOBr soln. for 3 hrs. (2) yields 2,4-dimethylbenzoic ac. [Beil. IX-531], cryst. from dil. MeOH, m.p. 126°. With a large excess of NaOBr and longer time (20 hrs.)  $\bar{C}$  yields 5-bromo-2,4-dimethylbenzoic acid. [Beil. IX-533], m.p. 180-181° (2).

$\bar{C}$  on oxidn. with alk.  $KMnO_4$  soln. gives (3) 2-methylterephthalic acid [Beil. IX-563], m.p. 325-330°, whose dimethyl ester has m.p. 73-74° (4).

$\bar{C}$  treated with nicotinic acid hydrazide metho-*p*-toluenesulfonate in alc. gives corresp. hydrazone, cryst. from 1:1 EtOH/ether, m.p. 196° cor. (5).

3:1355 (1) Kuncell, *Ber.* 30, 579 (1897). (2) Fisher, Grant, *J. Am. Chem. Soc.* 57, 718-719 (1935). (3) Jörländer, *Ber.* 50, 1460 (1917). (4) Lacourt, *Bull. soc. chim. Belg.* 39, 136-138 (1930). (5) Allen, Gates, *J. Org. Chem.* 6, 596-601 (1941).

—	<i>cis</i> $\beta$ -CHLOROACRYLIC ACID	$\begin{array}{c} \text{HC}-\text{Cl} \\ \parallel \\ \text{HC}-\text{COOH} \end{array}$	$\text{C}_3\text{H}_3\text{O}_2\text{Cl}$	Beil. II - 400 II <sub>1</sub> -(186) II <sub>2</sub> —
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M.P. 63-64°

See 3:2240 under *trans*- $\beta$ -chloroacrylic acid.

3:1364	DIETHYL <i>meso</i> - $\alpha,\alpha'$ -DICHLOROSUCCINATE	$\begin{array}{c} \text{COOC}_2\text{H}_5 \\   \\ \text{H}-\text{C}-\text{Cl} \\   \\ \text{H}-\text{C}-\text{Cl} \\   \\ \text{COOC}_2\text{H}_5 \end{array}$	$\text{C}_8\text{H}_{12}\text{O}_4\text{Cl}_2$	Beil. II - 619 II <sub>1</sub> — II <sub>2</sub> -(558)
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M.P. 63° (1) B.P. 125.5° cor. at 12.5 mm. (1)  $D_4^{20} = 1.1490$  (1)  
 61.75-62° (2)  $n_D^{24.5} = 1.4266$  (1)  
 57° (3)

Nds. from dil. alc.; very eas. sol. alc., ether. — Volatile with steam.

[For prepn. of  $\bar{\text{C}}$  from *meso*- $\alpha,\alpha'$ -dichlorosuccinic acid (3:4930) in EtOH with HCl gas see (2) (1); from diethyl fumarate with HOCl see (3).]

3:1364 (1) Kuhn, Wagner-Jauregg, *Ber.* 61, 485-486, 504 (1928). (2) Kirchhoff, *Ann.* 280, 214-215 (1894). (3) Henry, *Bull. acad. roy. Belg* (3) 36, 31-54 (1898); *Cent.* 1898, II 663.

3:1370	CHLOROACETIC ACID	$\begin{array}{c} \text{H}_2\text{C}-\text{COOH} \\   \\ \text{Cl} \end{array}$	$\text{C}_2\text{H}_3\text{O}_2\text{Cl}$	Beil. II - 194 II <sub>1</sub> -( 87) II <sub>2</sub> -(187)
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M.P. $\alpha$ -form	M.P. $\beta$ -form	M.P. $\gamma$ -form	B.P.		
63° (1) (2)	56.68° (99)	52.5° (10)	189.35°	at 760 mm.	(27) (90) (92)
(3) (4) (5) (6)	56.6° (16)	51° (25)	180°	at 771 mm.	(28)
62.80° (7)	(17)	50.65° (7)	189°		(12)
62.53° (8)	56.3° (7)	50.2° (22)	188.8-189.4°		(29)
62.5-63.2° (9)	(21) (99)	50.05° (23)	188.6-189.4°		(30)
62.5° (36)	56.18° (22)	50° (20)	188.5-189.5° cor.		(31)
62.3° (10)	56.01° (23)		187.8°	at 755.7 mm.	(32)
(11)	56° (2) (25)		186°	at 760 mm.	(33)
62.0-62.5° (9)	55° (20)		149°	at 207 mm.	(34)
62° (12) (13)			145.2°	at 180 mm.	(34)
(14) (15)			140.5°	at 152 mm.	(34)
61.86° (99)			139.0°	at 141 mm.	(34)
61.8° (16) (17)			135°	at 122 mm.	(34)
61.7° (18) (103)			130.1°	at 101 mm.	(34)
61.65° (99)			122°	at 71 mm.	(34)
61.5° (19) (20)			108°	at 36 mm.	(34)
(21)			102.5°	at 27 mm.	(34)
61.4° (100)			104-105°	at 20 mm.	(1)
(102) (104)			101°	at 20 mm.	(36)
61.30° (22)			93°	at 18 mm.	(34)
61.18° (23)			94°	at 11 mm.	(35)
61-62° (24)			85-86°	at 11 mm.	(2)
61° (19) (25)					
60-61° (26)					

[See also dichloroacetic acid (3:6208) and trichloroacetic acid (3:1150).]

MISCELLANEOUS PHYSICAL PROPERTIES OF  $\bar{C}$ 

Polymorphism of  $\bar{C}$ .  $\bar{C}$  is known definitely in the above three  $\alpha$ ,  $\beta$ , and  $\gamma$  forms and perhaps also in a fourth  $\delta$  form, m.p. 43.75° (23), although last could not be confirmed (22) cf. (7). — The stable ( $\alpha$ ) form results from rapid condensation of vapor (23), by crystallization of  $\bar{C}$  from aq. soln. (23), or from rapid cooling of fused  $\bar{C}$  (37), although last method could not be confirmed (25); it is also obtained from the  $\beta$  form by seeding with  $\alpha$  (9) or from  $\gamma$  form by spontaneous transformation (20), or from either  $\beta$  or  $\gamma$  forms at -20° (22).

The  $\beta$  form results from cooling fused  $\bar{C}$  especially if melt is first htd. above 67° cf. (9) (23), or from  $\gamma$  form on stirring (23) (20) (37) (22) cf. (25) (7).

The  $\gamma$  form results from fused  $\bar{C}$  on cooling without stirring (23) (20) (37) (25) (7).

[For study of transformation points of  $\alpha$  and  $\beta$  forms see (21); for studies of effect of pressure on m.p. of  $\bar{C}$  see (38) (39) (25) (8).]

Density and refractive index for fused  $\bar{C}$ . [Values for these constants are *not* in good accord, viz.,  $D_4^{65.4} = 1.3978$  (40),  $D_4^{65} = 1.3703$  (41);  $n_D^{65.4} = 1.4301$  (40),  $n_D^{65} = 1.4297$  (41). — For  $D_4^t$  over range 80°–176° see (36).]

Vapor characteristics. [For study of vapor pressure of  $\bar{C}$  over range 85–180° see (42). — For study of volatility with steam see (43).]

Cryoscopic constant. [Molal f.p. constant for  $\bar{C}$  is 5.2° (for 1000 g.  $\bar{C}$ ) (44) (37); for studies on use of  $\bar{C}$  as cryoscopic solvent see (44) (45) (46) (47).]

Association of  $\bar{C}$ . [For studies on extent of association of  $\bar{C}$  in  $C_6H_6$  soln. at 30° (11), in *p*-chlorotoluene (3:8287) (48), in liquid HF (49), in ether (33), or in water (1–9.7%  $\bar{C}$ ) (50) see indic. refs.]

Heat of combustion. [For studies on heat of combustion of  $\bar{C}$  see (51) (52) (53) (54) cf. (55).]

Exchange reactions. [For study of behavior of  $\bar{C}$  with  $D_2O$  see (56); with  $H_2O^{18}$  see (57).]

Adsorption of  $\bar{C}$  by various adsorbents. [For studies on adsorption of  $\bar{C}$  from aqueous solns. by various forms of carbon (58) (59) (60) (61) (62) (63) (64), by silica gel (60), by synthetic resins (65), by aniline black (66), by filter paper (67), by hide powder (68), by viscose (69), by  $Zr(OH)_2$  (70), or by  $Fe(OH)_3$  (71) see indic. refs.]

[For studies on adsorption of  $\bar{C}$  from nonaqueous solvents by wood charcoal (72) or from aqueous alc. by charcoal (73) or by casein (74) see indic. refs.]

Distribution of  $\bar{C}$  between solvents. [For data on distribution of  $\bar{C}$  between *aq.* and *ether* at 18° (75) or at 25° (76) (77) cf. (81); between *aq.* and *benzene* at 25° (78) or at an unstated temp. (79); between *aq.* and *toluene* at 25° (78) (80); between *aq.* and *isobutyl alcohol* at 25° (80); between *aq.* and *n-amyl alcohol* at 25° (80); between *aq.* and *isoamyl alcohol* at 25° (80); between *aq.* and *di-n-butyl ether* at 25° (5); between *aq.* and *olive oil* at 25° and 37.5° (82) see indic. refs.]

[For data on distribution of  $\bar{C}$  between *aq.* and *nitrobenzene* at 25° (80); between *aq.* and *mixts. of benzene + nitrobenzene* (83); between *aq.* and *o-nitrotoluene* at 25° (80) (84) see indic. refs.]

[For data on distribution of  $\bar{C}$  between *aq.* and  $CHCl_3$  (3:5050) at 25° (80) (85) (86); between *aq.* and  $CCl_4$  (3:5100) at 25° (80) (87) (85); between *aq.* and  $EtBr$  at 25° (80) (77); between *aq.* and  $CHBr_3$  at 25° (85); between *aq.* and  $MeI$  at 25° (80) (87) see indic. refs.]

[For data on distribution of  $\bar{C}$  between *aq.* and  $CS_2$  at 25° (85); between *aq.*  $MgSO_4$  or  $K_2SO_4$  solns. and *di-n-butyl ether* at 25° (88) (5); between *acetone* and *glycerol* at 25° (89) see indic. refs.]

BINARY SYSTEMS CONTAINING  $\bar{C}$ 

Azeotropic systems. [ $\bar{C}$  with *mesitylene* (1:7455) forms a const.-boilg. mixt., b.p. 162° at 760 mm., contg. 17 wt. %  $\bar{C}$  {90};  $\bar{C}$  with *naphthalene* (1:7200) forms a const.-boilg. mixt., b.p. 187.1° at 760 mm., contg. 78 wt. %  $\bar{C}$  {91};  $\bar{C}$  with *o-cresol* (1:1400) forms a const.-boilg. mixt., b.p. 187.5° at 760 mm., contg. 54 wt. %  $\bar{C}$  {91}.]

[ $\bar{C}$  with 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) forms a const.-boilg. mixt., b.p. 146.25° at 760 mm., contg. 1.8 wt. %  $\bar{C}$  {91};  $\bar{C}$  with pentachloroethane (3:5880) forms a const.-boilg. mixt., b.p. 158.65° at 760 mm., contg. 9.9 wt. %  $\bar{C}$  {91};  $\bar{C}$  with hexachloroethane (3:4835) forms a const.-boilg. mixt., b.p. 171.2° at 760 mm., contg. 25 wt. %  $\bar{C}$  {27};  $\bar{C}$  with 1,2,3-trichloropropane (3:5840) forms a const.-boilg. mixt., b.p. 154.5° at 760 mm., contg. 10 wt. % {92}.]

[ $\bar{C}$  with *p-dichlorobenzene* (3:0930) forms a const.-boilg. mixt., b.p. 167.55° at 760 mm., contg. 24.5 wt. %  $\bar{C}$  {27};  $\bar{C}$  with benzal (di)chloride (3:6327) forms a const.-boilg. mixt., b.p. 189.1° at 760 mm., contg. 97 wt. %  $\bar{C}$  {93}.]

[ $\bar{C}$  with *bromobenzene* forms a const.-boilg. mixt., b.p. 154.3° at 760 mm., contg. 11 wt. %  $\bar{C}$  {90};  $\bar{C}$  with *p-dibromobenzene* forms a const.-boilg. mixt., b.p. 186.3° at 760 mm., contg. 75 wt. %  $\bar{C}$  {93}.]

OTHER PHYSICAL DATA ON BINARY SYSTEMS CONTAINING  $\bar{C}$ 

$\bar{C}$  + aq. [ $\bar{C}$  is very eas. sol. aq. {32}; for study of hydration at low temps. see {94}; for f.p./compn. data see {23}. — Data on density of aq.  $\bar{C}$  is fragmentary but for  $D_{20}^{20}$  {40},  $D_{25}^{25}$  {95}, and  $D_{35}^{35}$  {95} for certain concns. see indic. refs. (cf. {96} {97} {98}). — For refractive indices of aq. solns. of  $\bar{C}$  see {20} {40} — For study of soly. of aq. in  $\bar{C}$  +  $C_6H_6$  see {103}.]

$\bar{C}$  +  $H_2SO_4$ . [For densities, viscosities, and elec. conductivity nt 20°, 40°, and 60° over whole compn. range see {12}; for f.p./compn. data over range 46–100%  $\bar{C}$  (no compound is formed) see {18}.]

$\bar{C}$  + acetic acid. (1:1010) [For f.p./compn. data and diag., eutectic m.p. -4.0°, contg. 22 mole %  $\bar{C}$ , see {99} cf. {100} {103} ]

$\bar{C}$  + dichloroacetic acid (3:6208). [For f.p./compn. data {100}, eutectic m.p. -10.5° contg. 30.7 mole %  $\bar{C}$  {101}, see indic. refs.]

$\bar{C}$  + trichloroacetic acid (3:1150). [For f.p./compn. data {100}, eutectic m.p. 17.5° contg. 48.5 mole %  $\bar{C}$  {101}, see indic. refs.]

$\bar{C}$  + miscellaneous organic compds. of Order 1. [For f.p./compn. data on following systems see indic. refs:  $\bar{C}$  +  $C_6H_6$  (1:7400) {103};  $\bar{C}$  + *naphthalene* (1:7200) {99} {17} {20};  $\bar{C}$  + *phenol* (1:1420) {17} {16} {102};  $\bar{C}$  + *o-cresol* (1:1400) {16} {102};  $\bar{C}$  + *m-cresol* (1:1730) {16};  $\bar{C}$  + *p-cresol* (1:1410) {16};  $\bar{C}$  +  $\alpha$ -*naphthol* (1:1500) {16};  $\bar{C}$  +  $\beta$ -*naphthol* (1:1540) {16};  $\bar{C}$  + *thymol* (1:1430) {16};  $\bar{C}$  + *guaiacol* (1:1405) {16};  $\bar{C}$  + *cetyl alc.* (1:5915) {99};  $\bar{C}$  + *meso-crythritol* (1:5825) {14};  $\bar{C}$  + *benzoic acid* (1:0715) {100};  $\bar{C}$  + *o-toluic acid* (1:0690) {100};  $\bar{C}$  + *m-toluic acid* (1:0705) {100};  $\bar{C}$  + *p-toluic acid* (1:0795) {100};  $\bar{C}$  + *phenylacetic acid* (1:0665) {100};  $\bar{C}$  + *cinnamic acid* (1:0735) {100};  $\bar{C}$  + *crotonic acid* (1:0425) {100};  $\bar{C}$  + *dimethyl oxalate* (1:0415) {103};  $\bar{C}$  + *dimethyl succinate* (1:3556) {103};  $\bar{C}$  + *methyl cinnamate* (1:2090) {103};  $\bar{C}$  + *phenyl salicylate* ("Salol") (1:1415) {99};  $\bar{C}$  + *piperonal* (1:0010) {99} {101};  $\bar{C}$  + *vanillin* (1:0050) {101};  $\bar{C}$  + *acetophenone* (1:5515) {101};  $\bar{C}$  + *benzil* (1:0015) {101};  $\bar{C}$  + *dibenzalacetone* (1:9021) {101} ]

$\bar{C}$  + miscellaneous compounds of Order 2. [For f.p./compn. data on following system see indic. refs.:  $\bar{C}$  + *urea* {19};  $\bar{C}$  + *ethyl carbamate* (urethane) {19}.]

TERNARY SYSTEMS CONTAINING  $\bar{C}$ 

[For f.p./compn. data and diag. of following systems see indic. refs.:  $\bar{C}$  ( $\alpha$ -form) + phenol (1:1420) + naphthalene (1:7200) (17);  $\bar{C}$  ( $\beta$  form) + phenol (1:1420) + naphthalene (1:7200) (17).]

USE OF  $\bar{C}$  IN FOODS AND BEVERAGES

**General.** [For discussion of use of  $\bar{C}$  as fermentation and oxidn. inhibitor or stabilizer in fruit juices, carbonated beverages, etc. (sometimes as "Esterex" (106)), see (106) (107) (108) (109) (110); for study of persistence of  $\bar{C}$  in such use see (111); for patents on such use see (112); for studies of bactericidal action (113) or fungistatic props. (114) of  $\bar{C}$  see indic. refs.]

**Toxicity of  $\bar{C}$ .** [For studies on toxicity of  $\bar{C}$  see (115) (116).]

**Detection and determination of  $\bar{C}$  in foods and beverages.** [For studies on detection and detn. of  $\bar{C}$  in commercial preservatives (624), in non-alc. beverages (117) (118) or in wines (119) (120) cf. (117) see indic. refs.; for identification of  $\bar{C}$  as  $Ba\bar{A}_2$  (optical and crystallographic props.) see (121) (623).]

PREPARATION OF  $\bar{C}$ 

**From acetic acid.** [For prepn. of  $\bar{C}$  from acetic acid (1:1010) by chlorination at 250-500° without cat. (625), with  $Cl_2$  in sunlight (32), in light from Hg quartz lamp (122), in silent electric discharge (123), or more usually in presence of catalysts (123) (124) (125) especially sulfur (124) (126) (127) (128) (129), red P (123) (124) (130), iodine (124), mixtures of red P +  $PCl_5$  +  $I_2$  (123) (124) (125) (131) (132) (133) (134), or in acetic anhydride (138) (139) at 100° or in vapor phase over  $NiCl_2$  at 350° (140) see indic. refs.]

[For prepn. of  $\bar{C}$  from acetic acid (1:1010) by chlorination with  $SO_2Cl_2$  at 115-120° and 4-5 atm. press. (135) or in pres. of a little acetyl chloride (136) or in presence of dibenzoyl peroxide in  $CCl_4$  (70% yield (137)) see indic. refs.; for formn. of  $\bar{C}$  from  $AcOH$  +  $HCl$  on electrolysis see (141).]

**From trichloroethylene.** [For prepn. of  $\bar{C}$  from trichloroethylene (3:5170) with conc.  $H_2SO_4$  at 190-195° see (142) (143) (144) (145) (146); for patents on this process see (147) (148) (149) (150) (151) (152) (153) (154). — Note also that  $H_2SO_4$  may be replaced by arom. sulfonic acids such as benzenesulfonic acid see (155). — Note also that a very similar process (156) starting from unsym.-tetrachloroethane (3:5555) doubtless first involves loss of  $HCl$  to trichloroethylene.]

**From other chloro-compounds.**  $\bar{C}$  is also formed by appropriate oxidation of many suitably constituted chloro-compounds [e.g., for formn. of  $\bar{C}$  from 1,2-dichloroethane (ethylene (di)chloride) (3:5130) with dry  $O_2$  in u.v. light see (157)].

[For formn. of  $\bar{C}$  by oxidation of unsaturated chloro-compds. see the following examples: 1,2-dichlorobutene-2, low-boilg. isomer (3:5360), high-boilg. isomer (3:5615) with  $KMnO_4$  in acetone (158); 1,4-dichlorobutene-2 (3:5725) with  $KMnO_4$  or  $O_3$  (159); 1,2,4-trichlorobutene-2 (3:9062) with aq.  $KMnO_4$  (160); 1,4-dichloro-2-methylbutene-2 (3:9204) with  $O_3$  followed by  $KMnO_4$  (161); 4-chlorobutadiene-1,2 (3:7225) with aq. alk.  $KMnO_4$  (162); 1,3-dichlorohexadiene-2,4 (3:9310) with aq.  $KMnO_4$  (163); 3,3,6-trichlorohexadiene-1,4 (3:9308) with aq.  $KMnO_4$  (164); 1,3,4,6-tetrachlorohexadiene-2,4 (3:9306) with aq.  $KMnO_4$  (164); 3,6-dichlorohexatriene-1,3,4 (3:9304) with aq.  $KMnO_4$  (164); 1-chloro-5-methoxypentadiene-2,3 with aq.  $KMnO_4$  (165); ethyl 5-chloropenten-3-oate with aq.  $KMnO_4$  (166); 1-chloro-5-methoxy-5-phenylpentene-2 with  $KMnO_4$  in acetone (35); chloroacetylene (3:7000) with  $NaOCl$  (167).]

[For formn. of  $\bar{C}$  from ethylene chlorohydrin (3:5552) by oxidn. with  $CrO_3$  (168); from

1-chloropropanol-2 (propylene  $\alpha$ -chlorohydrin) (3:7747) by oxidn. with  $\text{HNO}_3$ ; from 1,3-dichloropropanol-2 ("  $\alpha$ -dichlorohydrin ") (3:5985) by oxidn. with conc.  $\text{HNO}_3$  (169) cf. (170) see indic. refs.]

[For formn. of  $\bar{\text{C}}$  from chloroacetaldehyde (3:7212) by oxidn. with conc.  $\text{HNO}_3$  (171) cf. (172),  $\text{AgOH}$  (172) or dil.  $\text{H}_2\text{O}_2$  (173); from chloroacetone (3:5425) by oxidn. with  $\text{KMnO}_4$  (161) (174),  $\text{CrO}_3$  (174),  $\text{HNO}_3$  (174), (175); from 1-chlorohutanone-2 (3:8012) by oxidn. with  $\text{HNO}_3$  (176) (177) see indic. refs.]

From aminoacetic acid (glycine). [For formn. of  $\bar{\text{C}}$  from glycine with nitrous acid (40% yield (178)), with conc.  $\text{HCl}$  + conc.  $\text{HNO}_3$  (179), or from glycine hydrochloride with satd. aq.  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , or  $\text{ZnCl}_2$  +  $\text{NaNO}_2$  (180), see indic. refs.]

From miscellaneous sources. [For prepn. of  $\bar{\text{C}}$  from ketene with  $\text{Cl}_2$  in gas phase,  $\text{CCl}_4$ , or dry ether, followed by nq. (181); from ketene with nq.  $\text{Ca}(\text{OCl})_2$  (182); from formaldehyde +  $\text{CO}$  +  $\text{HCl}$  gas nt  $180^\circ$  and 800-900 atm. (183), for formn. of  $\bar{\text{C}}$  from  $\alpha$ -trioxymethylene with  $\text{SO}_2\text{Cl}_2$  in pres. of  $\text{ZnCl}_2$  or  $\text{AlCl}_3$  in s.t. at  $150^\circ$  for 12 hrs (2); from methyl formate (1:1000) with  $\text{SO}_2\text{Cl}_2$  in s.t. at  $165$ - $170^\circ$  (2); from ethylene with  $\text{ClO}_2$  (184); from nitro-trichloromethane ("chlorpicrin") in  $\text{AcOH}$  on exposure to light (185) cf. (186) (187) (188) ]

[For formn. of  $\bar{\text{C}}$  from  $\alpha,\beta$ -dichlorovinyl ethyl ether (3:5540) on boilg. with excess aq. see (189) (note, however, that with calcd. amt. nq. ethyl chloroacetate (3:5700) results (190)); for formn. of  $\bar{\text{C}}$  from unsym.-tetrachloroacetone (3:6085) by hydrolytic cleavage with aq.  $\text{KOH}$  see (191).]

[For formation of  $\bar{\text{C}}$  from its own derivatives, e.g., chloroacetyl chloride (3:5235), chloroacetic acid anhydride (3:0730), methyl chloroacetate (3:5585), ethyl chloroacetate (3:5700), or other esters, etc., see these compds.]

## CHEMICAL BEHAVIOR OF $\bar{\text{C}}$

### PYROLYSIS OF $\bar{\text{C}}$

[ $\bar{\text{C}}$  on distn. through a red-hot tube decomposes giving (192)  $\text{HCl}$  +  $\text{CO}$  +  $\text{CH}_2\text{O}$  (1:0145) + sym.-dichlorodimethyl ether (3:5245). —  $\bar{\text{C}}$  at  $250$ - $340^\circ$  over  $\text{ThO}_2$ , kuoilin, or animal charcoal gives (193)  $\text{HCl}$  +  $\text{CO}$  +  $\text{CO}_2$ , but  $\bar{\text{C}}$  merely boiled with activated carbon undergoes no decomposition (194).]

[ $\bar{\text{C}}$  on htg. in tertiary bases such as dimethylaniline (195) or pyridine (196) decomposes into  $\text{CO}_2$  +  $\text{MeCl}$  (3:7005), undoubtedly by way of formn. and decmpn. of intermediate quaternary ammonium compds. (betaines) (196).]

[ $\bar{\text{C}}$  in dry ether or  $\text{C}_6\text{H}_6$  soln. on exposure to ultra-violet light decomposes giving (197)  $\text{HCl}$  + fumaric acid (1:0895) + a substance which on shaking with nq. yields glycolide (1:0667).]

### REDUCTION OF $\bar{\text{C}}$

[ $\bar{\text{C}}$  on reduction in nq. or aq. alc. alk. with  $\text{H}_2$  in pres. of  $\text{Pd}$  or  $\text{Ni}$  (198) (199) (200), or  $\bar{\text{C}}$  with chromous sulfate (201), or  $\bar{\text{C}}$  with finely divided  $\text{Fe}$  (202), or  $\bar{\text{C}}$  in nq.  $\text{EtOH}$  in ultra-violet light (203), or  $\bar{\text{C}}$  on electrolytic reduction (204) gives acetic acid (1:1010). — Note, however, that attempts to effect bimolecular hydrogenation of  $\bar{\text{C}}$  to succinic acid have been unsuccessful (205).]

### OXIDATION OF $\bar{\text{C}}$

[ $\bar{\text{C}}$  on oxidn. with  $\text{K}_2\text{S}_2\text{O}_8$  gives (206) methylene (di)chloride (3:5020); for study of oxidn. of  $\bar{\text{C}}$  to  $\text{CO}_2$  with  $\text{K}_2\text{S}_2\text{O}_8$  see (207). —  $\bar{\text{C}}$  (as  $\text{NaA}$ ) on electrolysis gives (208) cf. (209) methylene (di)chloride (3:5020), chloromethyl chloroacetate [Beil. II-198, II-2-

(193)], and other prods. — For study of photochemical oxidn. of  $\bar{C}$  with  $KMnO_4$  in pres. of uranyl salts see (210).]

### REACTIONS INVOLVING SUBSTITUTION OF H ATOMS OF ALKYL RADICAL OF $\bar{C}$

**Fluorination.** The behavior of  $\bar{C}$  with  $F_2$  appears not to have been studied: chloro-fluoroacetic acid is unknown; chloro-difluoroacetic acid [Beil. II-201] although known has been prep'd. from difluoroacetic acid by chlorination.

**Chlorination.** [ $\bar{C}$  with  $Cl_2$  (211) in pres. of  $I_2$  (212) gives dichloroacetic acid (3:6206) very likely accompanied by some trichloroacetic acid (3:1150).]

**Bromination.** [ $\bar{C}$  with  $Br_2$  at  $160^\circ$  is claimed (213) to give chloro-bromo-acetic acid [Beil. II-217, II<sub>2</sub>-(204)], but this is best prepared by other means, e.g., from  $\alpha,\beta$ -dichloro-vinyl ethyl ether (3:5540) by addn. of  $Br_2$ , conversion by distn. to chloro-bromo-acetyl chloride, and hydrolysis (214) (41) (215) (216). — Note that although dibromination of  $\bar{C}$  to chloro-dibromo-acetic acid [Beil. II-220] appears unreported, yet this product is obt'd. by other means cf. (217).]

**Sulfonation.** [ $\bar{C}$  with  $ClSO_3H$  on warming (218) or  $\bar{C}$  with  $SO_3$  finally at  $70^\circ$  (219) cf. (220) gives sulfo-chloroacetic acid [Beil. III-598, III<sub>1</sub>-(208), III<sub>2</sub>-(387)], hygroscopic ndls. of monohydrate from aq., m.p.  $83^\circ$  (219) (corresp. bis-acid chloride, oil, b.p.  $70^\circ$  nt 3 mm.,  $D^{15}_D = 1.669$ ,  $n^{23}_D = 1.4920$  (121); corresp.  $N,N,N',N'$ -tetraphenyldiamide, m.p.  $210^\circ$  (121)), accompanied (218) (220) by some chloromethanedisulfonic acid (chloromethionic acid) [Beil. II-25]. — For resolution of *d,l*-sulfochloroacetic acid see (219).]

**Miscellaneous substitution reactions.** [ $\bar{C}$  (as  $K\bar{A}$ ) on heig. with  $Hg$  gives (222) the salt of chloromercuri-chloroacetic acid which with either acid or alk. gives glycolic acid (1:0430).]

### REACTIONS INVOLVING THE $-COOH$ GROUP OF $\bar{C}$

#### Acidic Strength of $\bar{C}$

$\bar{C}$  behaves as a very strong monobasic acid; Neut. Eq. = 04.5. — [Ionization const. of  $\bar{C}$  in aq. nt  $25^\circ$  is  $1.55 \times 10^{-3}$  (223) (224),  $1.51 \times 10^{-3}$  (224) (225),  $1.396 \times 10^{-3}$  (226),  $1.378 \times 10^{-3}$  (227). — For examples of other studies of ioniz. const. of  $\bar{C}$  in aq. see (228) (229); for study of temp. variation of ioniz. const. in aq. over range  $0-40^\circ$  see (227) (230); for  $H^+$  conc. of  $\bar{C}$  in aq. solns. (75), in aq. solns. of  $KCl$  or  $NaCl$  (231) (234), or in buffer mixts. of  $\bar{C} + Na\bar{A}$  (232) (233); for studies of elec. conductivity of  $\bar{C}$  in aq. soln. at  $0^\circ$  (235), at  $60^\circ$  (236), at  $62.5^\circ$  (45), or over range  $0-78^\circ$  (4) see indic. refs. — For discussion of resonance and acid strength of  $\bar{C}$  see (237) (238) (239). — For study of "sourness" of  $\bar{C}$  from taste aspect see (252).]

[Studies of acid strength of  $\bar{C}$  in other solvents include the following: in  $EtOH$  (240) (241), in *n*- $BuOH$  (24) (242), in 60% methyl "cellosolve" (ethylene glycol monomethyl ether) (243), in *m*-cresol (242), in ether (244), in formamide (245), in acetonitrile (246), in  $C_6H_6$  (247), in chlorobenzene (248), or in  $CHCl_3$  (244). — For studies on electrometric titration of  $\bar{C}$  in  $C_6H_6$  (249), or use of indicators with  $\bar{C}$  in  $C_6H_6$  soln. (250), see indic. refs. — For studies of elec. conductivity of  $\bar{C}$  in  $MeOH$ ,  $EtOH$ ,  $BuOH$ , acetone see (251).]

#### Catalytic Effect of $\bar{C}$ upon Various Reactions

The catalytic influence of  $\bar{C}$  upon diversified types of chem. reaction has been extensively examined; although this matter cannot be recorded exhaustively, the following examples are cited.

[For studies of catalytic effect of  $\bar{C}$  upon the inversion of *l*-menthone to *d*-isomenthone in  $C_6H_6$  (253) or in chlorobenzene (254); upon racemization of methyl-phenyl-acetophenone

and of isobutyl-phenyl-acetophenone in various solvents (255); upon  $I_2$ /acetone reaction (224) (234) (256) (257) (232); upon hydrogen disproportionation of limonene (622) see indic. refs.]

[For studies of catalytic effect of  $\bar{C}$  upon the hydrolysis of ethyl formate in neutral salt solns. at 25° (258); of EtOAc (259) (235) in pres. of Na $\bar{A}$  or NaCl (259) (225); of sucrose (260) (261) see indic. refs.]

[For studies of catalytic effect of  $\bar{C}$  upon formn. of ether from ethyl alcohol (262); upon depolymerization of paraldehyde (273) or of dimeric dihydroxyacetone (263); upon bromination of ethyl acetoacetate (264) see indic. refs.]

[For studies on catalytic effect of  $\bar{C}$  upon nitration of toluene (265) (266); upon decompn. of ethyl diazoacetate in  $C_6H_6$  (253) (267); upon decompn. of nitramide (268); upon rearr. of *N*-chloroacetanilide in chlorobenzene soln. at 100° (269); upon rearr. of *N*-bromoacetanilide in chlorobenzene,  $C_6H_6$ , or ethylene (di)chloride (270); upon rearr. of *N*-iodoformanilide in anisole (271); upon rearr. of *N*-bromobenzanilide in chlorobenzene at 25° (272) see indic. refs.]

### *Salts of $\bar{C}$*

This topic cannot be exhaustively treated here but following examples are cited.

Salts with inorganic bases. [NH $\bar{A}$ , from  $\bar{C}$  in abs. alc. with dry NH $_3$  gas (274). — Hydroxylamine salt, HONH $\bar{A}$ , cryst. from boilg. alc., m p. 124–125° (275).]

[Na $\bar{A}$  on electrolysis gives (203) (209) methylene (di)chloride (3:5020), chloromethyl chloroacetate [Beil. II-198, II- (193)], and other prods.; on htg. gives (276) polyglycolid, for rate of decompn. by aq. see (277). — K $\bar{A}$ , 3H $_2$ O (32); K $\bar{A}$  1/2H $_2$ O (32) (277) (for study of rate of decompn. by aq. see (277)); K $\bar{A}$ . $\bar{C}$ , sparingly sol. aq. (32). — Ag $\bar{A}$ , spar. sol. cold aq., more readily in hot aq. (32); for soly. in HNO $_3$  see (278); dry htg. gives (270) AgCl + polyglycolid; on htg. with a little aq. gives (279) AgCl + glycolic acid; for prepn. and study of activity coefficient in pres. of electrolytes see (280); for sensitivity to light see (281).]

[Ba $\bar{A}$ , see (293); Mg $\bar{A}$ .2H $_2$ O, very sol. aq. or alc. (277); Ca $\bar{A}$ .H $_2$ O, very sol. aq. or alc. (277) (for use in eel worm control in soil see (282)); Sr $\bar{A}$ , spar. sol. aq. alc. (277); Ba $\bar{A}$ .H $_2$ O (32) (277) (293) (for use in detn. of  $\bar{C}$  see (121) (623)); Cu $\bar{A}$ .4H $_2$ O (274), Cu $\bar{A}$ .3H $_2$ O (283), Cu $\bar{A}$ .2 (274) cf. (284); for study of electrolysis see (285); for dissoc. see (288); for various complexes with Ni $f_2$  and amines see (286) (287). — Zn $\bar{A}$ .2(47)H $_2$ O (274). — Cd $\bar{A}$ .6H $_2$ O, for prepn. (289), crystallography (290), dissociation (285), and conductivity (291) see indic. refs. — Pb $\bar{A}$ , spar. sol. cold aq. (274). — Hg $\bar{A}$ , spar. sol. aq. (292). — Hg $_2$  $\bar{A}$ , spar. sol. aq. (292).]

[Al $\bar{A}$ , see (293). — Mn $\bar{A}$ . $\bar{C}$ .H $_2$ O (274); Mn $\bar{A}$ . $\bar{C}$ .2H $_2$ O (274); Mn $\bar{A}$ .1.5H $_2$ O (289). — Co $\bar{A}$ .6H $_2$ O, m.p. 68–69° (289), for study of complexes with pyridine see (294). — Ni $\bar{A}$ .3H $_2$ O (274), for complexes with various amines see (295). — For studies on complexes of  $\bar{C}$  with iron salts see (274) (296) (297).]

Salts with organic bases (amines). [Aniline chloroacetate, m p. 88° (298) (best from  $\bar{C}$  in dry ether treated dropwise with aniline in dry ether with cooling (299); note that this salt with P $_2$ O $_5$  on stdg. gives (299) *o*-chloroacetanilide, m p. 136° cor.). — *o*-Toluidine chloroacetate, m.p. 95° (300). — *p*-Toluidine chloroacetate, m.p. 97.5° (300) (note that this salt at 80–90° for 2 hrs. (301) or with P $_2$ O $_5$  (302) gives chloroaceto-*p*-toluidide, m.p. 164° (302)).]

*o*-Phenylethylamine chloroacetate, from  $\bar{C}$  + base in EtOAc, m.p. 93.6–94.4° u.c., 91.7–93.5° cor. (303). — Benzylamine chloroacetate, from  $\bar{C}$  + base in EtOAc, m.p. 118.4–119.4° u.c., 119.0–120.9° cor. (303) (note that this m.p. is practically identical with corresponding benzylamine salt of trichloroacetic acid (3:1150) q.v.). — Piperazine bis-(chloroacetate), m.p. 145–146° cor. (304). — Semicarbazide chloroacetate, m.p. 111–112° (305).



*Phenylhydrazine chloroacetate*, from  $\bar{C}$  with phenylhydrazine in  $C_6H_6$ , m.p.  $111^\circ$  (306) (note that this product is definitely the salt since on titration with alk. it gives Neut. Eq. 204.7 as against calcd. value of 202.6 (306); however, during detn. of m.p. it is undoubtedly converted to chloroaceto-phenylhydrazide, m.p.  $115^\circ$  (307), directly obtd. from chloroacetyl chloride (3:5235) with phenylhydrazine in ether (307)).

### *Behavior of Acidic Hydrogen of $\bar{C}$ with Metals*

[For study of rate of soln. of Mg in aq. solns. of  $\bar{C}$  see (308); for behavior of  $\bar{C}$  with Zn see (309); for study of 20% aq. solns. of  $\bar{C}$  on silver see (310).]

### *Esterification of $\bar{C}$*

This book includes the following esters of  $\bar{C}$  under their own individual numbers q.v.: *methyl chloroacetate* (3:5585), *ethyl chloroacetate* (3:5700), *n-propyl chloroacetate* (3:0565), *isopropyl chloroacetate* (3:8160), *n-butyl chloroacetate* (3:8530), *isobutyl chloroacetate* (3:8375), *sec-butyl chloroacetate* (3:8350), *ter-butyl chloroacetate* (3:8220), *ethylene glycol (mono)-chloroacetate* (3:6780), *ethylene glycol bis-(chloroacetate)* (3:0720),  *$\beta$ -methoxyethyl chloroacetate* (3:0285), *diethylene glycol (mono)chloroacetate* (3:9390), *triethylene glycol (mono)-chloroacetate* (3:0583), and *phenyl chloroacetate* (3:0565).

[For studies of rate of esterification of  $\bar{C}$  under various conditions with MeOH (1:6120) (311) (312) (313) (314) (315), with EtOH (1:6130) (312) (313) (1) (316) (317) (318), with isobutyl alc. (1:6165) (310) (320), with amyl alc. (313), or with neopentyl alc. (1:5812) (321) see indic. refs. — For studies on esterification of  $\bar{C}$  with alcohols by  $BF_3$  method (312) (322) or without cat. (328) see indic. refs.]

[For patents involving esterification of  $\bar{C}$  with alcs. (323) by use of  $Cl_2$  (324) see indic. refs.]

[For study of use of  $\bar{C}$  in esterification of various carbohydrate derivs. (325) or of cellulose (320) cf. (327). — Note that the chemistry of poly (vinyl chloroacetate) cannot be considered here.]

### *Addition Reactions of $\bar{C}$ with Organic Compounds*

**Addition to unsaturated linkages.**  $\bar{C}$  in presence of suitable cat. adds to unsaturated linkages giving the corresp. esters [e.g.,  $\bar{C}$  with propylene +  $BF_3$  at  $60-70^\circ$  gives (34.2% yield (329)) isopropyl chloroacetate (3:8160);  $\bar{C}$  with butene-2 +  $ZnCl_2$  at  $100^\circ$  for 8 hrs. gives (330) *sec*-butyl chloroacetate (3:8350); similarly  $\bar{C}$  with pentene-2 (1:8215) gives (330) diethylcarbinyl chloroacetate, b.p.  $177-178^\circ$ . — Note, however, that no record can be found of reaction of  $\bar{C}$  with ethylene to give ethyl chloroacetate (3:5700)].

[ $\bar{C}$  with *n*-butylacetylene (hexyne-1) (1:8055) in pres. of  $HgO$  + MeOH +  $BF_3 \cdot Et_2O$  gives (68% yield (331)) 2-(chloroacetoxy)hexene-1, b.p.  $100-101^\circ$  at 20 mm.,  $D_{25}^{25} = 1.017$ ,  $n_D^{25} = 1.4453$  (331). (For addition of  $Br_2$  to this prod. giving 67% yield 1-bromohexanone-2 + 21% yield chloroacetyl bromide see (334)).]

**Addition to epoxy compounds.** [ $\bar{C}$  with ethylene oxide (1:6105) in dry ether at  $0^\circ$  for 4 days (332) or at  $50^\circ$  under press. for 0 days (333) gives ethylene glycol mono(chloroacetate) (3:6780).]

### *Conversion of $\bar{C}$ to Corresponding Acyl Halides*

**Conversion of  $\bar{C}$  to chloroacetyl fluoride.** [ $\bar{C}$  on distn. with fluorosulfonic acid (335) or  $\bar{C}$  with  $KF$  + benzoyl chloride (3:6240) (336) gives (yields: 30% (336), 15% (335)) chloroacetyl fluoride, h.p.  $74^\circ$  (335),  $74-76^\circ$  (336).]

**Conversion of  $\bar{C}$  to chloroacetyl chloride.** [ $\bar{C}$  can by numerous methods be converted

to chloroacetyl chloride (3:5235) q.v. — Note also, however, that  $\bar{C}$  with large excess  $PCl_5$  (4 moles) gives (337) tetrachloroethylene (3:5460) and other products.]

Conversion of  $\bar{C}$  to chloroacetyl bromide. [ $\bar{C}$  with  $Br_2$  + red P (338) (339) or with  $PBr_3$  (340) gives chloroacetyl bromide, b.p.  $127^\circ$  (338) (340),  $D_4^{20} = 1.840$  (340).]

#### *Conversion of $\bar{C}$ to Corresponding Anhydride*

$\bar{C}$  can by numerous methods be converted to chloroacetic acid anhydride (3:0730) q.v.

### REACTIONS INVOLVING THE CHLORINE ATOM OF $\bar{C}$

#### *Reduction of $\bar{C}$*

See above as second heading under *chemical behavior of  $\bar{C}$* .

#### *Hydrolysis of $\bar{C}$ (or its salts)*

Hydrolysis of  $\bar{C}$  to glycolic (hydroxyacetic) acid (1:0430) together with the form. under certain conditions of diglycolic acid (1:0495) has been very extensively studied.

Hydrolysis of  $\bar{C}$  (or its salts) with aq.  $\bar{C}$  on protracted boilg. with aq. (341) (342) (343) or  $\bar{C}$  (as  $Na\bar{A}$  or  $K\bar{A}$ ) on boiling with aq. (32) (344) (277) or  $\bar{C}$  with aq.  $BaCO_3$  (followed by pptn. of barium with  $H_2SO_4$  (345)) gives (88.7% yield (345)) glycolic acid (1:0430).

[For studies on rate of hydrolysis of  $\bar{C}$  by aq. under various conditions (326) (342) (343) (346) (347) (348) (349) (350) (351), for study of influence of ultra-violet light (352) (353) (354) (355); for influence of temperature (356); for study of ord. and in heavy aq. (357); for heat of hydrolysis with aq. (358); for study of abnormalities of hydrolysis of salts (359); for study of induction period of hydrolysis (360) (383); for acceleration of hydrolysis by colloidal  $Ag$ ,  $Ag_2O$ , or  $CuO$  (349) see indic. refs.]

[For studies of quantum yields of hydrolysis of  $\bar{C}$  and use as standard see (361) (362) (363) (364) (365) (366) (367) (353).]

Hydrolysis of  $\bar{C}$  (or its salts) with alkalis.  $\bar{C}$  on hydrolysis with aq. alkalis also gives glycolic acid (1:0430) [for studies of this reaction see (368) (342) (340) (369) (370) (350) (371) (351) (372) (373); for studies of hydrolysis of  $Na\bar{A}$  by salts of weak acids (374), for study of basic catalysts (375), for effect of high press. (376) see indic. refs.]

[For patents on conversion of  $\bar{C}$  to glycolic acid (1:0430) by alkaline hydrolysis see (377) (378); note, however, that the glycolic acid so formed may be converted (379) to glycolid (1:0667).]

Note also that under the influence of the alkaline medium some of the glycolic acid first formed may condense with unreacted  $\bar{C}$  to give diglycolic acid (1:0495); for studies of this aspect of the reaction see (380) (381) (382).

#### *Behavior of $\bar{C}$ with $NaSH$ or Its Relatives*

[ $\bar{C}$  with aq. 15%  $KSH$  (384) or with freshly prepd. aq. 15%  $NaSH$  (385) at  $95^\circ$  for 1 hr., subsequently acidified with  $H_2SO_4$  and extracted with ether, gives (99% yield (385)) mercaptoacetic acid (thioglycolic acid) [Beil. III-244, III<sub>1</sub>-(95), III<sub>1</sub>-(175)], b.p.  $107-108^\circ$  at 16 mm. (384) (385), m.p. =  $-16.5^\circ$  (384),  $D_{20}^{20} = 1.3253$  (384) — Note that this prod. is also preparable by many other methods some of which are cited below.]

[ $\bar{C}$  (2 moles) as  $Na\bar{A}$  with  $NaSH$  as directed (386) (387) (388), or as  $K\bar{A}$  with  $KSH$  (389) (390), or as  $Na\bar{A}$  with potassium sulfantimonite (391) or sodium sulfostannate (391), or as  $Ca\bar{A}_2$  with excess  $Ca(SH)_2$  +  $H_2S$  (381) gives (84% yield (387)) thiodiglycolic acid (thiodiacetic acid),  $S(CH_2COOH)_2$  [Beil. III-253, III<sub>1</sub>-(97), III<sub>2</sub>-(178)], cryst. from  $AcOEt/C_2H_5$  (1:9) (388) m.p.  $130^\circ$  (388),  $129^\circ$  (387) (386).]

[ $\bar{C}$  (2 moles) as  $\text{Na}\bar{A}$  with aq.  $\text{Na}_2\text{S}_2$  (392) (393) (394), with alk. or alk.-earth polysulfides (402), with sodium sulfantimonate  $\text{Na}_3\text{SbS}_4$  (391) or sodium sulfarsenate  $\text{Na}_3\text{AsS}_4$  (391) gives dithiodiglycolic acid,  $\text{HOOC}\cdot\text{CH}_2\text{—S—S—CH}_2\cdot\text{COOH}$  [Beil. III-254, III<sub>1</sub>-(97), III<sub>2</sub>-(179)], lfts. from  $\text{AcOEt}/\text{C}_6\text{H}_6$  (1:9) (388) 108–109° (391), 106° (388). — Note that this prod. on reduction gives mercaptoacetic acid (above): e.g., for reduction with  $\text{Sn} + \text{HCl}$  (395), with  $\text{Zn} + \text{H}_2\text{SO}_4$  (393) (396) (401) (402), with  $\text{Na}/\text{Hg}$  (397), by electrolytic reduction in  $\text{H}_2\text{SO}_4$  soln. using  $\text{Pb}$  electrodes (398), by shaking soln. of sodium salt with  $\text{Fe}$  powder at 38° under  $\text{N}_2$  (399), or by shaking with alanine or phenylalanine in 1% soln. in pres. of active carbon at 38° under  $\text{N}_2$  (400) see indic. refs.]

### *Behavior of $\bar{C}$ with Various Salts of Inorganic Acids*

(For behavior with  $\text{NaCN}$ , etc., see further below.)

With halides. [ $\bar{C}$  with  $\text{HBr}\cdot 5\text{H}_2\text{O}$  in a.t. at 150° gives (403) bromoacetic acid [Beil. II-213, II<sub>1</sub>-(95), II<sub>2</sub>-(201)], m.p. 49–50°, b.p. 208°; however,  $\bar{C}$  in aq.  $\text{KBr}$  at 50° shows only very slight tendency to formn. of bromoacetic acid (for study of equilibrium see (404)).]

[ $\bar{C}$  with aq.  $\text{KI}$  at 50° (405) (406), or  $\bar{C}$  with  $\text{NaI}$  in acetone at room temp. (407) (or in ethyl methyl ketone, diethyl ketone, or  $\text{AcOEt}$  (407) but *not* in  $\text{EtOH}$  (408)) gives iodoacetic acid, cryst. from much pet. ether (405) (409), m.p. 83° (405), 82° (406); for study of equilibrium of  $\bar{C}$  with  $\text{KI}$  in aq. at 50° see (404); of  $\bar{C}$  with  $\text{KI}$  or  $\text{NaI}$  in acetone (ionic reaction) see (410).]

With salts of inorganic sulfur, nitrogen, or phosphorus acids. [ $\bar{C}$  with aq.  $\text{Na}_2\text{SO}_3$  gives (41) (412) salts of sulfoacetic acid [Beil. IV-21, IV<sub>1</sub>-(312), IV<sub>2</sub>-(531)]; for study of rate of reaction of  $\text{K}\bar{A}$  with  $\text{Na}_2\text{SO}_3$ ,  $\text{K}_2\text{SO}_3$ , or  $(\text{NH}_4)_2\text{SO}_3$  under various conditions see (214) (413).]

[The salts of  $\bar{C}$  with aq.  $\text{Na}_2\text{S}_2\text{O}_3$  give the corresp. salts of "glycolic acid thiosulfate" (carboxymethyl hydrogen sulfato) [Beil. III-235, III<sub>1</sub>-(97), III<sub>2</sub>-(171)]; for studies of this reaction see (414) (415) (416) (417) (418).]

The alkali salts of  $\bar{C}$  with aq. alkali nitrites give the corresp. alkali salts of nitroacetic acid; in fact from a conc. aq. soln. of the potassium nitroacetate, treatment with the calcd. amt. of conc.  $\text{HCl}$  and extraction with much ether gives (70% yield (419)) (420) free nitroacetic acid [Beil. II-225, II<sub>1</sub>-(99), II<sub>2</sub>-(207)], m.p. 87–89° dec. (420). — However, even aq. solns. of the alkali salts of nitroacetic acid on warming readily lose  $\text{CO}_2$  yielding nitromethane [Beil. I-74, I<sub>1</sub>-(19), I<sub>2</sub>-(40)], b.p. 100.80–100.86° at 760 mm. (421), f.p. –29.2°,  $D_4^{25} = 1.1322$  (421),  $n_D^{25} = 1.38056$  (421), and although this product is now commercially available from other sources, the reaction is of considerable interest in connection with  $\bar{C}$ . — [For studies on the prepn. of nitromethane from  $\text{K}\bar{A} + \text{KNO}_2$  (yield 47% (422)) (423) (424) or from  $\text{Na}\bar{A} + \text{NaNO}_2$  (yields: 70% (428), 58% (426), 53% (429) (430) (431), 35–38% (425)) see indic. refs. — For studies on rate of decompn. of nitroacetic acid in aq. soln. at 20° (432), in  $\text{HCl}$ , or in acetate buffered solns. at 17.84° and 9.78° (433) cf. (434) (435) (436) see indic. refs.]

[The behavior of  $\bar{C}$  with  $\text{NaN}_3$  appears to be unreported; note, however, that ethyl chloroacetate (3:5700) with  $\text{NaN}_3$  gives (437) ethyl azidoacetate [Beil. II-229, II<sub>1</sub>-(101), II<sub>2</sub>-(208)], which upon hydrolysis with aq.  $\text{KOH}$  gives (437) azidoacetic acid.]

[For behavior of  $\bar{C}$  with aq.  $\text{Na}_3\text{PO}_4$  at 85° see (438).]

### *Behavior of $\bar{C}$ with Hydrocarbons*

$\bar{C}$  with certain aromatic hydrocarbons or their halogen derivs. at elevated temp. but without cat. condenses with elimination of  $\text{HCl}$  to give arylated acetic acids [e.g.,  $\bar{C}$  with



*Behavior of  $\bar{C}$  with Salts of Organic Acids*

With NaCN, KCN, etc. [ $\bar{C}$  on conversion to Na $\bar{A}$  and reaction with aq. NaCN (465) (466) (475) (476) or KCN (467) (468) (469) gives (yields: 75% (469), 70% (468)) cyanoacetic acid (malonic acid mononitrile) [Beil. II-583, II<sub>2</sub>-(253), II<sub>2</sub>-(630)], m.p. 69-70° (468), 69° (470), 66.1-66.4° cor. (467), 65-66° (471), 65° (472) (473); for use of this reaction in prepn. of malonic acid (1:0480) see (476).]

Note, however, that the behavior of  $\bar{C}$  or its salts with KSCN, NH<sub>4</sub>SeN, alkali xanthates, etc., is both complex and disputed and cannot be detailed here.

*Behavior of  $\bar{C}$  with NH<sub>3</sub>*

$\bar{C}$  with NH<sub>3</sub> under various conditions gives aminooacetic acid (glycine) [Beil. IV-333, IV<sub>1</sub>-(462), IV<sub>2</sub>-(771)].

[For behavior of  $\bar{C}$  with conc. aq. NH<sub>4</sub>OH as method of prepn. of glycine (yields: 66-69% (477), 64-65% (478), 54% (470), 50% (480)) (481) (482) (486) (for numerous older refs. see Beilstein) see indic. refs.: for extensive studies on influence of conditions on this reaction see (483) (477); for study of rate of ammonolysis of  $\bar{C}$  see (484) (485). — For behavior of  $\bar{C}$  with liq. NH<sub>3</sub> see (487); note that  $\bar{C}$  in liq. NH<sub>3</sub> with Na splits out calcd. amt. NaCl and that no cyanide is formed (488). — For behavior of  $\bar{C}$  with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> see (483) (477) (489).]

[Note that reaction of  $\bar{C}$  with NH<sub>3</sub> does not stop with formn. of aminooacetic acid (glycine) but that unchanged  $\bar{C}$  reacts with the latter to give (489) (490) (480) iminodiacetic acid ("diglycolamidic acid") HN(CH<sub>2</sub>COOH)<sub>2</sub> [Beil. IV-365, IV<sub>1</sub>-(481), IV<sub>2</sub>-(800)], and/or trimethylamine- $\alpha,\alpha',\alpha''$ -tricarboxylic acid ("triglycolamidic acid") [Beil. IV-369, IV<sub>1</sub>-(482), IV<sub>2</sub>-(801)], also obtd. from  $\bar{C}$  on fusion with ZnCl<sub>2</sub>/NH<sub>3</sub> (492).]

*Behavior of  $\bar{C}$  with Organic Amines*

With primary aliphatic amines. [ $\bar{C}$  with MeNH<sub>2</sub> as directed (497) gives (methylamino)-acetic acid (*N*-methylglycine = sarcosine) [Beil. IV-345, IV<sub>1</sub>-(468), IV<sub>2</sub>-(784)], but this prod. is usually prepd. in other ways. — Note, however, that  $\bar{C}$  (2 moles) with MeNH<sub>2</sub> (1 mole) + excess aq. NaOH gives (63-71% yield (493)) (494) methyliminodiacetic acid, CH<sub>3</sub>N(CH<sub>2</sub>COOH)<sub>2</sub> [Beil. IV-367, IV<sub>2</sub>-(800)], cryst. from aq. MeOH, m.p. 226-227° dec. (495), 226° dec. (496).]

[ $\bar{C}$  with excess aq. EtNH<sub>2</sub> as directed (498) gives ethylaminoacetic acid (*N*-ethylglycine) [Beil. IV-349, IV<sub>2</sub>-(787)], m.p. 180-182° dec. (499), 181.5° dec. (500). — The homologous *N*-alkylglycines appear never to have been prepared from similar reaction of  $\bar{C}$  with alkylamines, but for prepn. of *N*-(*n*-propyl)glycine [Beil. IV-352], m.p. 196-198° dec. (499), *N*-(isopropyl)glycine [Beil. IV<sub>2</sub>-(787)], *N*-(*n*-butyl)glycine, m.p. 192° (501), *N*-(isobutyl)glycine, m.p. 188° (501), or *N*-(*n*-amyl)glycine, m.p. 201° (501), by other methods see indic. refs.]

With secondary aliphatic amines. [ $\bar{C}$  with aq. Me<sub>2</sub>NH (502) (20) for 4 hrs. at 55° under press. (503) or with aq. *N*-aminoacetic acid (*N,N*-dihydro sec (505)). —  $\bar{C}$  with Et<sub>2</sub>NH similarly gives (506) *N,N*-diethylglycine [Beil. IV-350, IV<sub>1</sub>-(472).]

With tertiary aliphatic amines. [ $\bar{C}$  with Me<sub>3</sub>N (507) or  $\bar{C}$  (as Na $\bar{A}$ ) with Me<sub>3</sub>N (508) gives betaine hydrochloride (CH<sub>3</sub>)<sub>3</sub>N(Cl).CH<sub>2</sub>COOH [Beil. IV-347, IV<sub>1</sub>-(470), IV<sub>2</sub>-(786).]

With primary aromatic amines. (See also below under @'s.) [ $\bar{C}$  with aniline in a little ether boiled with a large volume of aq. (509), cf. (511), or  $\bar{C}$  with aniline (3 moles) boiled with aq. and subsequently made alkaline (510), or best  $\bar{C}$  with aq. aniline heated in pressure

of an acid acceptor such as aq. NaOH (512), aq. NaOAc (573) cf. (514), or other alkali or alkaline-earth hydroxides or carbonates (515) (516) (517) (518) (519) gives (yields: 100% (514), 90% (510), 86% (512)) phenylaminoacetic acid (*N*-phenylglycine) [Beil. XII-468, XII-(263)], m.p. 127° (note that if htd. at 200°, however, bimolecular condensation occurs with elimination of 2H<sub>2</sub>O and forma. (520) (521) of *N,N'*-diphenyl-2,5-diketopiperazine, m.p. 263° (520) (521) while distn. causes loss of CO<sub>2</sub> giving (522) *N*-methylaniline). — Note also that reaction of  $\bar{C}$  with 2 moles aniline (523), or further reaction of  $\bar{C}$  with *N*-phenylglycine (above) in aq. alk. (524) (525) (514) (526), gives (yields: 80–85% (526), 50–60% (525)) phenylimino-diacetic acid, C<sub>6</sub>H<sub>5</sub>N(CH<sub>2</sub>COOH)<sub>2</sub> [Beil. XII-480, XII-(265)], m.p. 152–155° dec. (526). — Note also that reaction of  $\bar{C}$  with aniline in pres. of NaOAc gives (525) much *N*-phenylglycine anilide, C<sub>6</sub>H<sub>5</sub>NIICH<sub>2</sub>CONH.C<sub>6</sub>H<sub>5</sub> [Beil. XII-556], m.p. 112°]

[Note that  $\bar{C}$  with many other primary aromatic amines reacts in analogous fashion, but details cannot be included here because of lack of space]

With primary aromatic diamines. [ $\bar{C}$  with *o*-phenylenediamine in dry ether forms (327) a 1:1 cpd presumably to be regarded as salt — However,  $\bar{C}$  (1 mole) with *o*-phenylenediamine (1 mole) in 4 *N* HCl refluxed (528) for 45 min and allowed to stand overnight (529) (530) gives (yields: 80–85% (529), 78–86% (530)) 2-(chloromethyl)benzimidazole, ndls. from EtOH/AcOEt (528), pr. from dioxane (529) or dry acetone (530), m.p. 165° (529), 160–161° (528), 159–160° cor (530), note that value is sensitive to rate of htg. (529) (530). — For studies of behavior of this product with many amines (529) (530), with aq. (530), KI in acetone (530) (531) see indic. refs. — For general study of ortho condensations leading to benzimidazole formn see (532)]

With hydrazines. [ $\bar{C}$  (1 mole) with phenylhydrazine (2 moles) in boilg. aq. alc. K<sub>2</sub>CO<sub>3</sub> ( $\frac{1}{2}$  mole) gives (533) (534) a mixt. of both ( $\alpha$ -phenylhydrazine)acetic acid, C<sub>6</sub>H<sub>5</sub>N(NH<sub>2</sub>).CH<sub>2</sub>COOH [Beil. XV-316], tbs. from abs. EtOH, m.p. 168° (533), 167° dec. (535), and ( $\beta$ -phenylhydrazine)acetic acid, C<sub>6</sub>H<sub>5</sub>NH.NHCH<sub>2</sub>COOH [Beil. XV-321], lfts. from alc., m.p. 153° (536), 152–153° (537); for separation of these isomers see (533).]

[For behavior of  $\bar{C}$  with *N,N*-diphenylhydrazine in aq. Na<sub>2</sub>CO<sub>3</sub> or NaOAc see (538).]

With aromatic primary amines also containing other functional groups. With amino-phenols. [ $\bar{C}$  with *p*-aminophenol on htg. in aq. soln. (539) (540) (541) (542) contg. also NaOAc (543) (544) gives (yields: 45% (544), 35% (539) *N*-(*p*-hydroxyphenyl)glycine [Beil. XIII-488, XIII-(171)] (this product has considerable interest as a photographic developer); for its purification see (540) (545); for pat. on its decomn. at 160–170° in ketone solvents as method of prepn. of *N*-methyl-*p*-aminophenol [Beil. XIII-441, XIII-(149)] see (546). — Note also that in above reaction of  $\bar{C}$  with *p*-aminophenol some *N*-(*p*-hydroxyphenyl)iminodiacetic acid (542) is also formed]

With amino acids. [ $\bar{C}$  with *o*-aminobenzoic (anthranilic) acid in aq. soln. (547) preferably also contg. Na<sub>2</sub>CO<sub>3</sub> (548) (549) (550) gives (yields: 85–89% (550), 70–80% (549)) *N*-(*o*-carboxyphenyl)glycine (phenylglycine-*o*-carboxylic acid) [Beil. XIV-348, XIV-(544)], ndls. from MeOH, m.p. about 215° dec (551); this product upon htg. loses CO<sub>2</sub> giving indoxyl and is therefore an important intermediate in mfg. of indigo; for use of this reaction for detection of  $\bar{C}$  in wine by conversion to indigo see (120) cf. (117) — Note also that in above reaction of  $\bar{C}$  with anthranilic acid some *N*-(*o*-carboxyphenyl)iminodiacetic acid [Beil. XIV-354, XIV-(545)], m.p. 216° dec. (551), is also produced (551); although both phenylglycine-*o*-carboxylic acid (Neut. Eq. 97.5) and *N*-(*o*-carboxyphenyl)iminodiacetic acid (Neut. Eq. 84.3) thus melt at same temp., their mixture melts at about 200° (551).]

With secondary aromatic amines. [ $\bar{C}$  with *N*-methylaniline on htg. (552) or better in aq. NaOH on 4-hr. reflux (553) gives (74% yield (553)) *N*-methyl-*N*-phenylglycine [Beil. XII-473, XII-(264)], oil (B.HCl, m.p. 215–216° dec. (553)). —  $\bar{C}$  with *N*-ethylaniline on

htg. gives (554) *N*-ethyl-*N*-phenylglycine [Beil. XII-475], oil. —  $\bar{C}$  with diphenylamine at 180–200° for 40–50 hrs. gives (5–10% yield (555)) *N,N*-diphenylglycine [Beil. XII- (264).]

With tertiary aromatic amines. [ $\bar{C}$  with dimethylaniline at 100° (556) for 12–18 hrs. (557) gives dimethyl-phenylbetaine hydrochloride [Beil. XII-474], m.p. 194–196° (556), from which silver oxide liberates (557) (558) free dimethyl-phenylbetaine, m.p. 124–126° (557), 123–124° (558). — For corresp. betaine from *N,N*-diethylaniline see (559).]

With tertiary heterocyclic amines. [ $\bar{C}$  with pyridine on htg. (560) (561) (194) cf. (556) at 60° for 5 hrs. (557) gives *N*-(carboxymethyl)pyridinium chloride (pyridohetaine hydrochloride) [Beil. XX-226], m.p. 202–205° dec. (560) (thought by (194) to be typographical error for 102–105° dec.). — For behavior of  $\bar{C}$  with quinoline see (556).]

#### *Behavior of $\bar{C}$ with Amides, Thioamides, etc.*

This topic cannot here be treated in full, but the following cases are reported as examples.

With urea. [ $\bar{C}$  with carhamide (urea) might be expected under appropriate conditions to condense with elimination of HCl and formn. of ureidoacetic acid (hydantoic acid),  $\text{NH}_2\text{CONH}\cdot\text{CH}_2\text{COOH}$  [Beil. IV-359, IV<sub>1</sub>-(477), IV<sub>2</sub>-(792)], m.p. 169–170° (562) (563), 160–161° (564), 160° (565), or its ring-closure product hydantoin [Beil. XXIV-242, XXIV<sub>1</sub>-(287)], m.p. 220°; no report of the chemical behavior of  $\bar{C}$  with urea can be found, however, the two above-mentioned expected products having been prepared by other means. — Note that f.p./compn. data on system  $\bar{C}$  + urea have been recorded (19).]

With thiourea. [ $\bar{C}$  with thiourea (the latter reacting in its isothiurea mode) gives according to conditions either isothiohydantoic acid,  $\text{H}_2\text{N}-\text{C}(=\text{NH})-\text{S}-\text{CH}_2\cdot\text{COOH}$  [Beil. III-251, III<sub>1</sub>-(97)] (566) (567), or pseudothiohydantoin [Beil. XXVII-233, XXVII<sub>1</sub>-(303)], (568) (569) (570) (571) (572) (573).]

With substituted thioureas. The behavior of  $\bar{C}$  with substituted thioureas cannot be treated in full, but the following examples are cited [for reaction of  $\bar{C}$  with various monosubstituted thioureas see (573) (574), with various disubstituted thioureas see (575) (576) (577)].

— Methyl chloroacetate: oil, b.p. 131° (see 3:5585).

— Ethyl chloroacetate: oil, b.p. 144° (see 3:5700).

— Phenyl chloroacetate: m.p. 44–45° (see 3:5565).

— *o*-Tolyl chloroacetate: oil, b.p. 127–127.6° at 10 mm. (578). [From  $\bar{C}$  with *o*-cresol (1:1400) +  $\text{POCl}_3$  in pyridine (574), or from chloroacetyl chloride (3:5235) with *o*-cresol (1:1400) at 130° for 4 hrs. (578); note that this prod. with  $\text{AlCl}_3$  at 140° undergoes Fries rearr. giving (578) both 2-hydroxy-3-methylphenacyl chloride [Beil. VIII<sub>1</sub>-(549)], m.p. 67°, and 4-hydroxy-3-methylphenacyl chloride [Beil. VIII<sub>1</sub>-(550)], m.p. 144–145°.]

— *m*-Tolyl chloroacetate: oil, h.p. 153° at 30 mm. (580). [From chloroacetyl chloride (3:5235) with *m*-cresol (1:1730) (579) (580); note that this prod. with  $\text{AlCl}_3$  at 150° gives (50% yield (580)) 2-hydroxy-4-methylphenacyl chloride [Beil. VIII-113, VIII<sub>1</sub>-(550)], m.p. 101°.]

— *p*-Tolyl chloroacetate: m.p. 32° (580), 29–30° (579); h.p. 162° at 45 mm. (580);  $D_4^{35} = 1.1840$  (41),  $n_D^{35} = 1.5150$  (41). [From  $\bar{C}$  with *p*-cresol (1:1410) +  $\text{POCl}_3$  in pyridine (579), or from chloroacetyl chloride (3:5235) with *p*-cresol (1:1410) at 135° (580); note that this prod. with  $\text{AlCl}_3$  at 140° gives (580) 2-hydroxy-5-methylphenacyl chloride [Beil. VIII-111], m.p. 65° (580).]

— Benzyl chloroacetate: oil, h.p. 147.5° at 9 mm.,  $D_4^4 = 1.2223$ ,  $n_D^{18} = 1.5246$  (581). [From  $\bar{C}$  with benzyl alc. (1:6480) + HCl gas at 100° (581).]

- *p*-Nitrobenzyl chloroacetate: oil, unsuitable as  $\Phi$  (582).
- Phenacyl chloroacetate: unreported.
- *p*-Chlorophenacyl chloroacetate: unreported.
- $\Phi$  *p*-Bromophenacyl chloroacetate: m.p. 103.7° cor. (583).
- *p*-Iodophenacyl chloroacetate: unreported.
- $\Phi$  *p*-Phenylphenacyl chloroacetate: m.p. 116° (581). [From  $\bar{C}$  (as Na $\bar{A}$ ) with *p*-phenylphenacyl bromide (584) (m.p. 121.5–125.5°) in aq. alc. on htg. (581).]
- $\Phi$  *S*-Benzylthiuronium chloroacetate: m.p. 159–160° (585). [Note that for corresp. salts from dichloroacetic acid (3:6205) and trichloroacetic acid (3:1150) m.p. values are respectively 178–179° and 148–149° (585).]
- $\Phi$  *S*-(*p*-Chlorobenzyl)thiuronium chloroacetate: m.p. 158° cor. (586). [From  $\bar{C}$  (as Na $\bar{A}$ ) with *S*-(*p*-chlorobenzyl)thiuronium chloride (586) (m.p. 197°) in alc. (586); note that corresp. deriv. of trichloroacetic acid (3:1150) has m.p. 148° cor.]
- $\Phi$  *S*-(*p*-Bromobenzyl)thiuronium chloroacetate: m.p. 151° cor. (587). [From  $\bar{C}$  (as Na $\bar{A}$ ) with *S*-(*p*-bromobenzyl)thiuronium bromide (587) (m.p. 213°) in alc. (587); note that corresp. deriv. of trichloroacetic acid (3:1150) has m.p. 146° cor. (587).]
- $\Phi$   $\omega$ -Chloroacetamide: m.p. 120.5–121.5° (588), 120° (589), 119–120° (590), 119.5° (591), 118–120° (165), 118° (312), 116.4–116.9° (620). [From methyl chloroacetate (3:5385) (588) (593) or ethyl chloroacetate (3:5700) (590) (589) (592) (591) (595) (596) (597) with cold conc. NH $_4$ OH (78–84% yield (590)), or from chloroacetyl chloride (3:5235) with dry NH $_3$  (597).]
- $\Phi$   $\omega$ -Chloroacetanilide: cryst. from hot aq. or 50% alc., m.p. 138° cor. (598), 136–137° (599), 136° cor. (600), 135° (601), 134–135° (602) (166), 134.5° (603) (604), 131° (605) (606), 133–134° (610). [From  $\bar{C}$  with aniline (606) in presence of P $_2$ O $_5$  (600) (603), from  $\bar{C}$  with aniline salts + PCl $_3$  or SOCl $_2$  (607), from chloroacetyl chloride (3:5235) with aniline (2 moles) in ether (608) (604), C $_6$ H $_6$  (602) (601), or AcOH/NaOAc (599) or with aniline (1 mole) + aq. NaOH in C $_6$ H $_6$  or toluene (609), or from chloroacetic acid anhydride (3:0730) with aniline + P $_2$ O $_5$  (610).] Note that this  $\omega$ -chloroacetanilide with AlCl $_3$  (not more than 1.8 pts (611): at 225° (611) (612) loses HCl with ring closure giving (85% yield (611) (612)) oxindole [Beil. XXI-282, XXI-1-(289)]; also that  $\omega$ -chloroacetanilide with alc. KOH undergoes bimolecular condensation giving (613) *N,N'*-diphenyl-2,5-diketopiperazine, m.p. 261°].
- $\Phi$   $\omega$ -Chloroacet-*o*-toluidide: cryst. from dil. alc., m.p. 111–112° (614) (604), 111° (615). [From  $\bar{C}$  + *o*-toluidine + P $_2$ O $_5$  (615), or from chloroacetyl chloride (3:5235) with *o*-toluidine (2 moles) in dry ether (616) or C $_6$ H $_6$  (611).] [Note that this prod. with AlCl $_3$  at 225° loses HCl with ring closure giving (612) 7-methyloxindole, m.p. 200°, also that with alc. KOH it undergoes bimolecular condensation giving (614) *N,N'*-di-*o*-tolyl-2,5-diketopiperazine.]
- $\Phi$   $\omega$ -Chloroacet-*p*-toluidide: m.p. 161° (615), 162° (608) (617), 161.5° (603). [From  $\bar{C}$  (2 moles) with *p*-toluidine (1 mole) at 80–90° (617) in presence of P $_2$ O $_5$  (615), or from chloroacetyl chloride (3:5235) with *p*-toluidine (2 moles) (608) in ether (613).] [Note that this prod. with AlCl $_3$  at 250° for 2 hrs. loses HCl with ring closure giving (612) 5-methyloxindole [Beil. XXI-291], m.p. 168° (612).]
- $\omega$ -Chloroacet-*N*-benzylamide: cryst. from C $_6$ H $_6$  or lgr., m.p. 91.5–91.5° cor. (618), 90.0–91.6° cor. (619), 92.2–92.8° u.c. (619). [From ethyl chloroacetate (3:5700) with aq. benzylamine on shaking in cold (619) cf. (621), or from chloroacetyl chloride (3:5235) with benzylamine + aq. KOH (618); note, however, that the corresp. derivs. from dichloroacetic acid (3:6208) and from trichloroacetic acid (3:1150) have also at the same m.p.'s, viz., 91.8–91.6° cor. and 91.6–91.4° cor. respectively (619), note also that the simple salt of  $\bar{C}$  with benzylamine has m.p. 119.9–120.9° cor. (591).]



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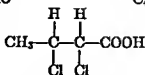
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3:1375  $\alpha,\beta$ -DICHLORO-*n*-BUTYRIC  
ACID (low-melting isomer)  
(Crotonic acid dichloride)

 $C_4H_6O_2Cl_2$ 

Beil. II - 279  
II<sub>1</sub>-(124)  
II<sub>2</sub>—



M.P. 63°	(1) (2)	B.P. 132-133° cor. at 27 mm. (5)
	(3) (6)	124.5° at 20 mm. (6)
62.5-63°	(4)	
62°	(8)	124-125° at 20 mm. (1)
61°	(11)	120° at 13 mm. (9)
57-59°	(5)	

[See also  $\alpha,\beta$ -dichloro-*n*-butyric acid (high-melting isomer) (isocrotonic acid dichloride) (3:1903).]

Colorless cryst. from pet. ether, lgr. or dry ether. —  $\bar{C}$  is eas. sol. alc.,  $C_6H_6$ ,  $CHCl_3$ , or  $CS_2$ ; spar. sol. cold lgr.; at 10.5° 3.28 pts.  $\bar{C}$  are sol. in 1 part dry ether. —  $\bar{C}$  deliquesces with a little aq. (5);  $\bar{C}$  with 1 mole  $H_2O$  forms (4) an oil, probably a monohydrate (ortho acid), which in much aq. gives an emulsion gradually separating into two clear layers; note, however, that  $\bar{C}$  has later (11) been claimed to be nonhygroscopic.

[For prepn. of  $\bar{C}$  from crotonic acid (1:0425) with  $Cl_2$  in  $CS_2$  (1) (2) (3) (4) (11) or in  $CCl_4$  +  $CS_2$  (6) in cold see indic. refs.; for formn. of  $\bar{C}$  from isocrotonic acid (1:1045) with  $Cl_2$  in  $CHCl_3$ ,  $CCl_4$ , or  $CS_2$  see (6) (4); for prepn. of  $\bar{C}$  from its corresp. acid chloride (see below) by hydrolysis with aq.  $NaHCO_3$  see (5) (9).]

$\bar{C}$  boils at 212-216° under ord. press. with some loss of  $HCl$  (4).

[ $\bar{C}$  with 6 pts. conc. aq.  $HCl$  (satd. at 0°) in s.t. at 100° for 50 hrs. (1) is partially isomerized to the high-melting stereoisomer (isocrotonic acid dichloride) (3:1903).]

$\bar{C}$  behaves as a fairly strong monobasic acid of ionization const.  $K = 3.2 \times 10^{-3}$  (1);  $\bar{C}$  with dil. aq.  $AgNO_3$  ppts. the spar. sol.  $Ag\bar{A}_2$  (5); no other salts, however, appear to have been reported.

$\bar{C}$  with aq.  $NaOH$  in cold is neutralized without serious decomposition (4); Neut. Eq. = 157 (11); however, if to the resulting soln. further conc. aq.  $NaOH$  is added (4) (7), or if  $\bar{C}$  in alc. is treated with alc.  $KOH$  (6) (2), 1  $HCl$  is split away and the corresp. salt of  $\alpha$ -chloroisocrotonic acid (3:1615) (accompanied by the salt of its isomeric  $\alpha$ -chlorocrotonic acid (3:2760)) is formed.

$\bar{C}$  with aq.  $Na_2CO_3$  at ord. temp. is neutralized without decompn. (4); however,  $\bar{C}$  with excess aq.  $Na_2CO_3$  above 80° also is further attacked giving (4) (25-30% yield (4)) 1-chloropropene-1 (3:7030), accompanied by some propionaldehyde (1:0110),  $\alpha$ -chlorocrotonic acid (3:2760),  $\alpha$ -chloroisocrotonic acid (3:1615), and other products.

$\bar{C}$  in pyridine at 100° for 3 hrs. loses  $HCl$  giving (yield not reported (8))  $\alpha$ -chlorocrotonic acid (3:2760), m.p. 99.5° (8).

[ $\bar{C}$  with  $PCl_5$  or  $SOCl_2$ , although not actually reported, would be expected to yield the corresp. acid chloride; this  $\alpha,\beta$ -dichloro-*n*-butyryl chloride, b.p. 163.3-164.3° cor. at 747 mm. (5), 67.5-71° at 30 mra. (5), has, however, been prepd. indirectly from crotonic acid (1:0425) with  $PCl_5$  (2 moles) at 160° for 2 hrs. (9) or from crotonaldehyde (1:0150) with  $Cl_2$  at 0° in dark (5).]

— Methyl  $\alpha,\beta$ -dichloro-*n*-butyrate: b.p. 174-180° sl. dec. at ord. press. (5), 82.7-85.7° cor. at 28 mm. (5);  $D_4^{18.3} = 1.2614$  (5). [From the above  $\alpha,\beta$ -dichloro-*n*-butyryl chloride with  $MeOH$  (5).]

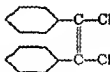
— Ethyl  $\alpha,\beta$ -dichloro-*n*-butyrate: b.p. 180-200° at 760 mm. (10), 97° at 35 mm. (10), 96° at 35 mm (2). [From  $\bar{C}$  in abs. EtOH with dry HCl (2), or indirectly from butyrylchloral hydrate (3:1905) (1 mole) in EtOH with dry KCN (1 mole) below 15° (10); note, however, that this ester loses HCl with great ease even at ord. temp. giving ethyl  $\alpha$ -chloroacetate (3:8523) and this dehydrohalogenation is greatly accelerated by KCN (10)]

—  $\alpha,\beta$ -Dichloro-*n*-butyramide: unreported. [Note that the amide from the higher-melting stereoisomer of  $\bar{C}$  (3:1003) has m.p. 121°.]

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(11) Stelling, *Z. physik. Chem.* B-24, 427 (1934).

3:1380 *cis*-1,2-DICHLORO-1,2-DIPHENYLETHYLENE  
(*cis*- $\alpha,\alpha'$ -Dichlorostilbene;  
*cis*-tolane dichloride)



$C_{14}H_{10}Cl_2$

Beil. V - 634  
V<sub>1</sub>-(304)  
V<sub>2</sub>—

M.P. 63° (1) (2) (3) B.P. 178° at 13 mm. (5)

(4) (5) (6)  
(7) (8)

62-63° (9)

62° (10)

61° (11)

60° (12)

59.5-60° (13)

58° (14)

[See also *trans*-1,2-dichloro-1,2-diphenylethylene (3:4210).]

Colorless ndls —  $\bar{C}$  is much less sol. in alc. than its higher-melting stereoisomer (3:4210); 100 pts. abs. alc. at 24.4° dis. 10-51 pts.  $\bar{C}$  (14). —  $\bar{C}$  like its isomer is very sol. in ether.

Note that  $\bar{C}$  (the lower-melting tolane dichloride) has now been shown (12) to have the *cis* configuration, many earlier reports to the contrary notwithstanding.

Note also that  $\bar{C}$  (2 moles) with (1 mole) diphenylacetylene (tolane) [Beil. V-656, V<sub>1</sub>-(319), V<sub>2</sub>-(568)], m.p. 60°, gives (12) a 2:1 molecular cpd., m.p. 67-69° (12).

$\bar{C}$  on distn. is partially transformed (32% (14)) into its higher-melting *trans* stereoisomer (3:4210) q.v.

Since the methods of prepn. and the chemical behavior of  $\bar{C}$  are the same as those given in detail under its stereoisomer (3:4210) q.v. they are not repeated here.

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**3:1385 1,7-DICHLORONAPHTHALENE**  
(2,8-Dichloronaphthalene)



$C_{10}H_8Cl_2$  Beil. V - 543  
V<sub>1</sub>-(263)  
V<sub>2</sub>-(446)

M.P. 64°	(19)	B.P. 286° u.c.	(5)	$D_4^{99.5} = 1.2611$	(19)
63.5-64.5°	(1)	285-286°	(2)	$n_D^{99.5} = 1.60921$	(19)
63.5-64°	(2)				
62.5°	(3) (18)				
61.5° u.c.	(4) (5) (9)				
	(12) (13)				
61°	(8) (12)				

Lfts. from hot dil. alc.; cryst. from alc., ether,  $C_6H_6$ , or AcOH. — Sublimes readily. — Volatile with steam.

[For prepn. of  $\bar{C}$  from 7-chloronaphthalenesulfonyl chloride-1 [Beil. XI-161] (4), from 7-bromonaphthalenesulfonyl chloride-1 [Beil. XI-166] (6), from 1-chloronaphthalenesulfonyl chloride-7 [Beil. XI-181] (2), from 7-chloro-1-nitronaphthalene [Beil. V-556] (poor yield (2)) (7), from 1-nitronaphthalenesulfonyl chloride-7 [Beil. XI-187] (8) (9) (10) (11), from 7-chloronaphthol-1 [Beil. VI-612, VI<sub>1</sub>-(308)] (12), from K or Na naphthol-2-sulfonate-8 [Beil. XI-286, XI<sub>1</sub>-(67)] (5) (13), or from naphthalene-1,7-bis-(sulfonyl chloride) [Beil. XI-215] (14) on htg. with  $PCl_5$  as directed see indic. refs.: from  $\alpha$ -chloronaphthalene (3:6878) with  $SO_2Cl_2$  at 100-180° see (15); from K 4,5-dichloronaphthalenesulfonate-2 [Beil. XI-182] or from K 4,6-dichloronaphthalenesulfonate-2 [Beil. XI-182] on hydrolysis in  $H_2SO_4$  or  $H_3PO_4$  with superhdt. steam see (16); from 4,6-dichloronaphthalene-2-sulfonyl chloride [Beil. XI-182] on htg. with conc. HCl in s.f. nt 200° see (16); from 7-chloronaphthylamine-1 [Beil. XII-1256] via diazotization and htg. with  $Cu_2Cl_2$  see (12); from 8-sulfonaphthylamine-2 [Beil. XIV-750, XIV<sub>1</sub>-(733)] via diazotization and htg. the diazonium salt with  $PCl_5$  in  $PCl_3$  see (2); from 1,7-diaminonaphthalene [Beil. XIII-204] via tetrazotization and treatment with Cu pdr. see (17).]

$\bar{C}$  (1 g.) in AcOH (5 ml.) with highest concn.  $HNO_3$  (2 ml.) yields (3) 1,7-dichloro- $\alpha$ -nitronaphthalene [Beil. V-556], ndls. from MeOH, m.p. 138-139° (3).

[ $\bar{C}$  with  $ClSO_3H$  yields (1) (18) 1,7-dichloronaphthalenesulfonic acid-4 [Beil. XI-162] (corresp. sulfonyl chloride, m.p. 118° (1) (18), corresp. sulfonamide, m.p. 226° (18)).]

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3:1400 1,3,5-TRICHLOROBENZENE  
(*sym.*-Trichlorobenzene)

 $C_6H_3Cl_3$ 

Beil. V - 204

V<sub>1</sub>-(43)V<sub>2</sub>-(156)

M.P. 63.0-63.8°	(1)	B.P. 208.5° cor. at 763.8 mm.	(2)
63.5° cor.	(2)	208.4°	(11)
	(3) (18)		
63.4° cor.	(4)		
63°	(5) (6)		
	(7) (8)		
62.7°	(9)		
61°	(10)		

Colorless cryst.; cas sol. ether,  $C_6H_6$ , lgr,  $CS_2$ ; spar. sol. cold alc. or 50% AcOH; volatile with steam. [For thermal anal. of mixts. of  $\bar{C}$  with 1,2,4-trichlorobenzene (3:6420) or for m.p./compn. data on ternary system of  $\bar{C}$  with 1,2,3-trichlorobenzene (3:0990) and 1,2,4-trichlorobenzene (3:6420) see (9)]

[For use of  $\bar{C}$  in msg. of electric insulating material see (12) (13).]

[For prepn. of  $\bar{C}$  from 2,4,6-trichloroaniline [Beil. XII-627, XII<sub>1</sub>-(312)] via diazotization and reaction with alc. (yield: 92% (14), 90% (15), 72.6% (8), 67% (33)) (4) (1) (16) (17), or from 2,4,6-tribromoaniline [Beil. XII-663, XII<sub>1</sub>-(329)] via diazotization and subsequent treatment with HCl gas in alc. (18), see indic. refs.; from 3,5-dichloroaniline [Beil. XII-626, XII<sub>1</sub>-(312)] via diazotization and reaction with  $Cu_2Cl_2$  or Cu (yield 58% (5), 40-50% (9)) (4) see indic. refs.; from chlorobenzene-3,5-disulfonyl chloride with 4 moles  $PCl_5$  in s.t. at 200-210° for 4 hrs. (60% yield (6)) or similarly from bromobenzene-3,5-disulfonyl chloride (7) see indic. refs.]

[For formn. of  $\bar{C}$  from 2,4,6-trichloroiodobenzene with alc. NaOEt see (19); from 1,3,5-trinitrobenzene with conc. HCl in s.t. at 260° see (20); from 2,4,6-trichloroacetophenone on fusion with KOH (10) or from 2,4,6-trichlorobenzaldehyde on warming with 50% NaOH or KOH (3) see indic. refs.; from chloroacetylene (3:7000) by polymerization in light see (21), for formn. of  $\bar{C}$  from  $C_6H_6$  or chlorobenzene (3:7903) with  $Cl_2$  at 400-700° (22), or from mixt. of *m*- and *p*-dichlorobenzenes with  $Cl_2 + AlCl_3$  (23) cf. (24), or from hexachlorobenzene (3:4939) by cat. hydrogenation (25) see indic. refs.; from  $\alpha$ -benzene-hexachloride (3:4410) with alc. KOH, pyridine, or quinoline (9) from  $\beta$ - or  $\gamma$ -benzene-hexachlorides with alc. KOH see (9) cf. (26)]

[ $\bar{C}$  with  $Cl_2$  in pres. of Al/Hg yields (27) 1,2,3,5-tetrachlorobenzene (3:0915); for behavior of  $\bar{C}$  with liq.  $Cl_2$  yielding addn. products see (28)]

[ $\bar{C}$  with MeOH/NaOMe in s.t. at 180° yields mainly (29) 3,5-dichloroanisole, m.p. 39° (29), accompanied by some 3,5-dichlorophenol (3:1670).]

[ $\bar{C}$  on hydrolysis with steam at 550-800° over cat yields (30) phloroglucinol (1:1620); for behavior of  $\bar{C}$  with  $P_2$  see (31); for behavior of  $\bar{C}$  with  $NH_3$  at 700-800° see (32).]

$\bar{C}$  on mononitration, e.g., by warming  $\bar{C}$  (1 g) with 5 ml fuming  $HNO_3$  ( $D = 1.49$ ) at 100° for 15 min., then pouring onto ice (38), gives (2) (8) (100% yield (38)) 1,3,5-trichloro-2-nitrobenzene [Beil. V-247], ndis. from alc., m.p. 69° (8), 67-68° (38). —  $\bar{C}$  on dinitration, e.g., by refluxing for 1 hr. a soln. of  $\bar{C}$  (1 g.) in 5 ml. fuming  $HNO_3$  ( $D = 1.49$ ) + 5 ml. conc.  $H_2SO_4$  (38), gives (yield: 100% (38) (34), 82% (35), 80% (15)) (14) (33) 1,3,5-trichloro-2,4-dinitrobenzene [Beil. V-265], m.p. 131-131.5° (35) (36), 129-130° (34), 128.5° (14) (15) (3), 128.5° (38) (this prod. on htg. with 5 pts. aniline yields (38) 1,3,5-trianilino-2,4-dinitrobenzene, m.p. 179-180° (38)). —  $\bar{C}$  on trinitration, e.g., by boilg. 2 days with mixt. of

fumg.  $\text{HNO}_3$  and fumg.  $\text{H}_2\text{SO}_4$  as directed (37) (39), yields (37) (33) (17) 1,3,5-trichloro-2,4,6-trinitrobenzene [Beil. V-275], m.p.  $187^\circ$  (33),  $193^\circ$  (15),  $192-193^\circ$  (39).

$\bar{\text{C}}$  with conc.  $\text{H}_2\text{SO}_4$  is unchanged even after htg. 56 hrs. at  $100^\circ$  and is only partially sulfonated on htg. 6 hrs. at  $100^\circ$  with fumg.  $\text{H}_2\text{SO}_4$  (12%  $\text{SO}_3$ ) (16); however,  $\bar{\text{C}}$  with 3 pts. fumg.  $\text{H}_2\text{SO}_4$  ( $\text{SO}_3 = 72\%$ ) htd. at  $100^\circ$  for 15 hrs. completely sulfonates yielding (16) 1,3,5-trichlorobenzene-2,4-disulfonic acid (corresp. disulfonyl chloride, m.p.  $161.5^\circ$  (16), corresp. disulfonamide, m.p.  $248^\circ$  (16)).

$\bar{\text{C}}$  with chlorosulfonic acid in  $\text{CHCl}_3$  (38) gives 1,3,5-trichlorobenzenesulfonyl chloride, m.p.  $35-40^\circ$  u.c. (38); this prod. with  $(\text{NH}_4)_2\text{CO}_3$  readily yields (38) 1,3,5-trichlorobenzene-sulfonamide, m.p.  $210-212^\circ$  u.c. dec. (38).

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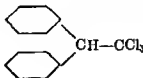
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3:1420 1,1,1-TRICHLORO-2,2-  
DIPHENYLETHANE



$\text{C}_{14}\text{H}_{11}\text{Cl}_3$

Beil. V - 606

V<sub>1</sub>-(285)

V<sub>2</sub>-(510)

M.P.  $64^\circ$  (1) (2) (3)

$63-64^\circ$  (5)

Colorless lfts. from alc. — 100 pts. 90-92% alc. dis. at room temp. 5.40 pts.  $\bar{\text{C}}$ ; in hot 37.28 pts.  $\bar{\text{C}}$  (4).

[For prepn. of  $\bar{\text{C}}$  from chloral (3:5210) with  $\text{C}_6\text{H}_6$  (2 moles) + conc.  $\text{H}_2\text{SO}_4$  (almost quant. yield) see (3); from chloral hydrate (3:1270) with  $\text{C}_6\text{H}_6$  + a little  $\text{AlCl}_3$  at  $0^\circ$  see (5) cf. (2); note that both types of this same condensation take place through intermediate formn. of trichloromethyl-phenyl-carbinol [Beil. VI-476, VI<sub>1</sub>-(237)], m.p.  $37^\circ$ , b.p.  $145^\circ$  at 15 mm. (1) (corresp. acetate, m.p.  $87.5^\circ$  (1)) as formerly suspected (6) and subsequently confirmed (1).]

$\bar{\text{C}}$  on reduction gives various products according to conditions [e.g.,  $\bar{\text{C}}$  with  $\text{Na/Hg}$  in

alc. is claimed (7) to give 1,1-diphenylethane [Beil. V-605,  $V_1$ -(285),  $V_2$ -(509)], but this prod. was not obtd. in pure form and was accompanied by 1,1-dichloro-2,2-diphenylethylene (3:1938) (from  $\bar{C}$  by loss of HCl under alk. conditions)].

[ $\bar{C}$  in boilg. 95% alc. contg. trace of  $CuCl_2$  with finely powdered Al/Cu/Zn (Devarda) alloy or Cu/Mg (Arnd) alloy for 6-10 hrs. gives (13-19% yield (8)) 2,2,3,3-tetrachloro-1,1,4,4-tetraphenylbutane [Beil.  $V_2$ -(676)], ndls from AcOH, m.p. 188-190° (8), accompanied by some 2,3-dichloro-1,1,4,4-tetraphenylbutene-2 (see next paragraph).  $\bar{C}$  with Zn dust + conc. aq.  $NH_4OH$  in alc. soln gives (18) (4) stilbene (1:7250) + 1,1-diphenylethane (above).]

[ $\bar{C}$  on reduction with  $H_2$  in pres. of Pd/ $BaCO_3$  in alc./pyridine soln. gives (54-60% yield (9)) 2,2,3,3-tetrachloro-1,1,4,4-tetraphenylbutane (see preceding paragraph) accompanied by both high-melting (137-138°) and low-melting (108-110°) stereoisomers of 2,3-dichloro-1,1,4,4-tetraphenylbutene-2 [Beil.  $V_2$ -(685)]; using Ni as cat. the same prods. result (9) in lower yield sometimes accompanied also by 1,1-dichloro-2,2-diphenylethylene (3:1938) (from  $\bar{C}$  by loss of HCl)]

[ $\bar{C}$  on reduction by electrolytic means in various types of solution, with various metallic electrodes, and at various temperatures gives (10) (11) numerous products including 1,1-dichloro-2,2-diphenylethane (3:1938), 1-chloro-2,2-diphenylethane [Beil. V-606,  $V_1$ -(285)], 1,1,4,4-tetraphenylbutene-2 [Beil.  $V_1$ -(379),  $V_2$ -(694)], etc.; for details see (10) (11).]

[ $\bar{C}$  with  $Cl_2$  under suitable conditions should give 1,1,1,2-tetrachloro-2,2-diphenylethane [Beil. V-606], m.p. 85°, but this reaction has not actually been reported — However,  $\bar{C}$  with a very large excess (15 pts.) pure liquid  $Br_2$  gives (12) 2-bromo-1,1,1-trichloro-2,2-diphenylethane, m.p. 87.5° (12)]

[No mono- or di-nitration products derived from  $\bar{C}$  have been reported.]

$\bar{C}$  on distillation (13), or on boilg. with alc. KOH (2) (14) (for study of rate see (15)), or during course of other reactions involving alkaline conditions (see above) loses HCl giving 1,1-dichloro-2,2-diphenylethylene (3:1938), m.p. 80° (2).

[ $\bar{C}$  with NaOEt in a.t. at 180° ultimately gives (2) cf. (16) (and presumably through intermediate 1,1-dichloro-2,2-diphenylethylene (3:1938)) diphenylacetic acid (1:0705).]

$\bar{C}$  with Na in  $C_6H_6$  refluxed 10-12 hrs. and then treated with alc. gives (17) cf. (2) *trans*-1,2-diphenylethylene (stilbene) (1:7250), m.p. 124°, *cis*-1,2-diphenylethylene (isostilbene) [Beil. V-633,  $V_1$ -(303),  $V_2$ -(539)], and diphenylacetylene (tolano) [Beil. V-656,  $V_1$ -(319),  $V_2$ -(568)]. —  $\bar{C}$  with Zn dust on dry distn. gives (13) stilbene (1:7250).

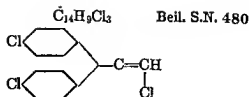
[ $\bar{C}$  in  $C_6H_6$  with  $AlCl_3$  gives (10% yield (20)) 1,1,2,2-tetraphenylethane [Beil. V-739,  $V_1$ -(371),  $V_2$ -(673)], m.p. 211°.]

[For use of  $\bar{C}$  as addn. agent to improve lubricating power of mineral oils under high pressures see (19).]

3:1420 (1) Chattaway, Muir, *J. Chem. Soc.* 1934, 701-703 (2) Harris, Frankforter, *J. Am. Chem. Soc.* 48, 3144-3150 (1926). (3) Baeyer, *Ber.* 5, 1098-1099 (1872). (4) Elbs, *J. prakt. Chem.* (2) 47, 45-46, 77 (1893). (5) Frankforter, Kritchewsky, *J. Am. Chem. Soc.* 36, 1515-1518 (1914). (6) Dinesmann, *Compt. rend.* 141, 201 (1905). (7) Goldschmidt, *Ber.* 6, 1502-1503 (1873). (8) Brand, *Ber.* 64, 1995-1996 (1921). (9) Brand, Horn, *J. prakt. Chem.* (2) 115, 359-362 (1926). (10) Brand, *Z. Elektrochem.* 16, 669 (1910); *Ber.* 64, 2017 (1921).

(11) Brand, *Ber.* 46, 2935-2942 (1913). (12) Schlenk, *Ann.* 493, 213 (1912). (13) Goldschmidt, *Ber.* 6, 987, 990 (1873). (14) Baeyer, *Ber.* 6, 223 (1873). (15) Brand, Busse-Sunder-

3:1430 1-CHLORO-2,2-bis-  
(*p*-CHLOROPHENYL)ETHYLENE



M.P. 64-65° (1)

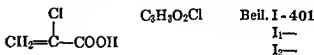
Cryst. from lgr. — Note that  $\bar{C}$  may occur as a minor impurity in technical grade "DDT" (3:3298).

[For prepn. of  $\bar{C}$  from "*p,p'*-DDD" (3:3320) by elimination of 1 HCl with alc. KOH (77% yield) see (1).]

$\bar{C}$  on oxidn. with  $CrO_3$  gives (84% yield (1)) 4,4'-dichlorobenzophenone (3:4270).

3:1430 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1600 (1945).

3:1445  $\alpha$ -CHLOROACRYLIC ACID



M.P. 65° u.c. (1) (4)

64-66° (7)

64-65° (2) (3) (6)

Cryst. from pet. ether (2), ndls. from ether (1). — Eas. volatile, subliming even at room temp. (1) (4); volatile with steam.

[For prepn. of  $\bar{C}$  from  $\alpha,\alpha$ -dichloropropionic acid (3:6162) with alc. KOH see (4); from methyl  $\alpha,\beta$ -dichloropropionate (3:9103) with aq.  $Ba(OH)_2$  (62% yield (2)) (1) or alc. KOH (5) see indic. refs.; from  $\alpha$ -chloro- $\beta$ -hydroxypropionic acid ( $\alpha$ -chlorohydroxyacrylic acid) [Beil. III-298] by distn. with  $H_2SO_4$  see (6) (7); from trichloroethylene (3:5170) with formaldehyde or paraformaldehyde +  $H_2SO_4$  as directed see (3).]

$\bar{C}$  on treatment with  $Ag_2O$  dec. yielding (1)  $Ag$  +  $AgCl$ .

$\bar{C}$  with fumg. HCl in s.t. at 100° yields (5) (4)  $\alpha,\beta$ -dichloropropionic acid (3:0855), m.p. 50°.

[The esters of  $\bar{C}$  (usually prepd. from the corresp. alkyl  $\alpha,\beta$ -dichloropropionates by elimination of HCl) have assumed special importance because of their ability to polymerize to useful resins; for methyl  $\alpha$ -chloroacrylate see 3:9096; for ethyl  $\alpha$ -chloroacrylate see 3:9242; for *sec*-butyl  $\alpha$ -chloroacrylate, and its mechanism of polymerization, see (8) (9); for studies on the electrical properties of  $\beta$ -chloroethyl  $\alpha$ -chloroacrylate see (10).]

$\bar{C}$  readily polymerizes in ultra-violet light or in pres. of peroxides (2).

3:1445 (1) Werigo, Werner, *Ann.* **170**, 168-171 (1874). (2) Marvel, Dec, Cooke, Cowan, *J. Am. Chem. Soc.* **62**, 3495-3498 (1940). (3) Imperial Chem. Ind., Ltd., French 845,230, Aug. 16, 1939; *C.A.* **35**, 1070 (1941); *Brit.* 528,761, Nov. 6, 1940; *C.A.* **35**, 7975 (1941). (4) Otto, Beckurts, *Ber.* **18**, 241-246 (1885). (5) Werigo, Melikov, *Ber.* **10**, 1499-1500 (1877). (6)

## 3:1460 3,4-DICHLOROPHENOL



Beil. VI - 190

VI<sub>1</sub>-(103)VI<sub>2</sub>-(179)M.P. 65° (1) (3)  
68° (2)

B.P. 253.5° at 767 mm. (2)

Ndls. (from  $\text{C}_6\text{H}_6$  by addn. of pet. ether (2)). — Volatile with steam (1). [For study of ionization const. see (4)]

Prepn. from 3,4-dichlorotoluene (3:1460) by oxidation on see (2) (3) (5) (1).] (2-chloroquinizarin)

[B at 195-200° see (7)]  
(8); for use of  $\bar{\text{C}}$  in prepn. of tetrachlorofluoran [Beil. XIX-148], m p. 255°, by hgt. with phthalic anhydride see (3).]

$\bar{\text{C}}$  dis. eas. in conc.  $\text{H}_2\text{SO}_4$ ; on stdg. small pl. of 3,4-dichlorophenol-6-sulfonic acid separate; these are sol. in aq., alc., AcOH, EtOAc; insol. in  $\text{C}_6\text{H}_6$ , pet. eth.; spar. sol.  $\text{CHCl}_3$ ; cryst. from latter, m p. 75-76° (6).

$\bar{\text{C}}$  on hgt. with mixt. of fuming  $\text{H}_2\text{SO}_4$  (25%  $\text{SO}_3$ ) + conc.  $\text{H}_2\text{SO}_4$ , and resultant solid treated with conc.  $\text{HNO}_3$  ( $D = 1.5$ ) as directed (1) gives (69% yield (1)) of 3,4-dichloro-2-nitrophenol, yel. ndls., from lt. pet. ether, m p. 76° (1).

$\bar{\text{C}}$  dislvd. in 3 pts. AcOH contg. anhyd. NaOAc, treated with  $\text{Cl}_2$  and the prod. pptd. by addn. of aq., yields (5) 2,3,4-trichlorophenol (3:2185)

$\bar{\text{C}}$  dislvd. in aq. NaOH and shaken with  $(\text{CH}_3)_2\text{SO}_4$  yields (2) the methyl ether, 3,4-dichloroanisole, m p. -8° (2).

3:1460 (1) Hodgson, Kershaw, *J. Chem. Soc.* 1929, 2922. (2) Holleman, *Rec. trav. chim.* 37, 102-104 (1918). (3) Badische Anilin- und Soda-Fabrik, Ger. 156,333, Nov. 14, 1904; *Cent.* 1904, II 1673. (4) Murray, Gordon, *J. Am. Chem. Soc.* 67, 110-111 (1935). (5) Groves, Turner, Sharp, *J. Chem. Soc.* 1929, 523. (6) Kraay, *Rec. trav. chim.* 48, 1084-1085 (1930). (7) Gubelmann, Lee (to Newport Co.), U.S. 1,655,462, Jan. 10, 1928, *Cent.* 1929, I 3149. (8) Gubelmann, U.S. 1,655,863, Jan. 10, 1928, *C.A.* 22, 966 (1928).

## 3:1475 3,5-DICHLOROBENZALDEHYDE



Beil. S.N. 635



M.P. 65° (1)

B.P. 235-240° at 748 mm. (1)

Colorless ndls. or lfts. from pet. ether or dil. MeOH (1). — Spar. sol. hot aq. but eas. volatile with steam — Eas. sol. most organic solvents.

[For prepn. of  $\bar{\text{C}}$  from 3,5-dichlorotoluene (3:6310) via chlorination to 3,5-dichlorobenzal (di)chloride (3:0370) and subsequent hydrolysis with conc.  $\text{H}_2\text{SO}_4$  (70-80% overall yield) see (1) (4).]

$\bar{\text{C}}$  with satd. aq.  $\text{NaHSO}_3$  yields a epd.  $\bar{\text{C}}$   $\text{NaHSO}_3$ ; this is exceptionally sol. in aq., and on hgt. the soln. yields  $\bar{\text{C}}$  (1)

$\bar{\text{C}}$  on oxidn. with excess  $\text{KMnO}_4$  at 100° gives (74% yield (1)) 3,5-dichlorobenzoic acid (3:4840), m p. 188° (1). —  $\bar{\text{C}}$  with 50% aq. KOH for 4 hrs. at 100° gives (90% yield (1)) 3,5-dichlorobenzyl alc., cryst. from  $\text{C}_6\text{H}_6$ , m p. 82° (1), and 3,5-dichlorobenzoic ac. (90% yield (1)) (3:4840).



$\bar{C}$  with  $PCl_5$  gives (80% yield (1)) 3,5-dichlorobenzal (di)chloride (3:0370) cryst. from MeOH or dil. AcOH, m.p. 36.5° (1).

$\bar{C}$  on nitration with fumg.  $HNO_3$  ( $D = 1.48$ ) at 0° as directed (2) gives (99% yield (2)) 3,5-dichloro-2-nitrobenzaldehyde, cryst. from AcOH or lgr., m.p. 91.5° (2), 91° (4). [This deriv. yields an oxime, m.p. 07°, a phenylhydrazone, m.p. 175°, and on oxidn. with  $KMnO_4$  gives 3,5-dichloro-2-nitrobenzoic ac., m.p. 194° cor. (2).]

$\bar{C}$  htd. with  $NaOAc + Ac_2O$  for 18 hrs. at 180-210° gives (76% yield (1)) 3,5-dichlorocinnamic acid, ndls. from  $C_6H_6 +$  pet. eth. or from dū. AcOH, m.p. 176° cor. (1).

[For conversion of  $\bar{C}$  to 3,5-dichlorostyrene (5) (6) in a reaction with MeMgI giving (yields: 69% (5), 55% (3)) 3,5-dichlorophenyl-methyl-carbinol, m.p. 46° (3), b.p. 126° at 4 mm. (5),  $n_D^{20} = 1.5573$  (5), and dehydration of latter with  $KHSO_4$  (43% yield (5)) see indic. refs.]

③ 3,5-Dichlorobenzaldoxime: cryst. from lgr.,  $C_6H_6 +$  pet. eth., or dil. AcOH, m.p. 112° (1).

④ 3,5-Dichlorobenzaldehyde phenylhydrazone: yel. ndls. from pet. eth., m.p. 106.5° (1).

—— 3,5-Dichlorobenzaldehyde *p*-nitrophenylhydrazone: unrecorded.

—— 3,5-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.

—— 3,5-Dichlorobenzaldehyde semicarbazone: unrecorded.

3:1475 (1) Asinger, Lock, *Monatsh.* 62, 344-348 (1933). (2) Asinger, *Monatsh.* 63, 386-387 (1934). (3) Lock, Böck, *Ber.* 70, 922-923 (1937). (4) Ruggli, Zaeslin, Lang, *Helv. Chim. Acta* 21, 1247 (1938). (5) Marvel, Overberger, Allen, Johnston, Saunders, Young, *J. Am. Chem. Soc.* 68, 864 (1946). (6) Michalek, Clark, *Chem. & Eng. News* 22, 1559-1563 (1944).

### 3:1480 2,3-DICHLOROBENZALDEHYDE

 $C_7H_4OCl_2$ 

Beil. S.N. 635



M.P. 65-67° (1)

Cryst. from 1:1 aq. EtOH.

[For prepn. of  $\bar{C}$  from 2,3-dichlorotoluene (3:6345) by bromination at 180-200° (presumably to 2,3-dichlorobenzal (di)bromide) followed by hydrolysis with conc.  $H_2SO_4$  at 100-140° (71% yield) see (1).]

$\bar{C}$  with MeMgI gives (76% yield (1)) 2,3-dichlorophenyl-methyl-carbinol, m.p. 55-57°, b.p. 112-113° at 2 mm. (corresp. 3,5-dinitrobenzoate, m.p. 145-146° (1)); note that dehydration of the carbinol with  $KHSO_4$  gives (44% yield (1)) 2,3-dichlorostyrene.

—— 2,3-Dichlorobenzaldoxime: unreported.

—— 2,3-Dichlorobenzaldehyde phenylhydrazone: unreported.

—— 2,3-Dichlorobenzaldehyde *p*-nitrophenylhydrazone: unreported.

—— 2,3-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

—— 2,3-Dichlorobenzaldehyde semicarbazone: unreported.

3:1480 (1) Marvel, Overberger, Allen, Johnston, Saunders, Young, *J. Am. Chem. Soc.* 68, 862 (1946).

## 3:1490 2-CHLORONAPHTHOL-1

 $C_{10}H_7OCl$ 
 Beil. VI - 611  
 VI<sub>1</sub>-(308)  
 VI<sub>2</sub>-(581)

M.P. 65° (1)

64-65° (2)

Ndls. from lgr.; exceptionally easily sol. in alc, ether,  $C_6H_6$ . — More volatile with steam than the isomeric 4-chloronaphthol-1 (3:3720) (use in sepn. (2)).

[For prepn. of  $\bar{C}$  from  $\alpha$ -naphthol (1:1500) with aq. alk.  $NaOCl$  (3) (4) (5) or with  $SO_2Cl_2$  in  $CHCl_3$  soln. (18% yield, together with 42% yield of 4-chloronaphthol-1 (3:3720) (2)), see indic. refs.; from sodium 1-hydroxynaphthalenesulfonate-2 [Beil. XI-269, XI<sub>1</sub>-(63)] with  $PCl_5$  see (6); from 2-chloro-1-hydroxynaphthalenesulfonic acid-4 (1) by hydrolysis in boilg. dil.  $H_2SO_4$  see (1)]

$\bar{C}$  on stdg. in aq.  $Na_2CO_3$  soln. gives blue flocks (7).

$\bar{C}$  with 1 mole  $Br_2$  in 20%  $AcOH$  yields alm. quant. (7) 4-bromo-2-chloro-naphthol-1, ndls., m.p. 112° (7).

[ $\bar{C}$  with conc.  $HI$  ( $D = 1.5$ ) in boilg.  $AcOH$  for 12 hrs. reduces (4) to  $\alpha$ -naphthol (1:1500), but  $\bar{C}$  is unaffected by  $SnCl_2 + HCl$  in alc. even after 28 hrs. 'boilg. (4)]

[ $\bar{C}$  on oxidn. with  $p$ -diamines gives (3) indophenols;  $\bar{C}$  on coupling with diazonium salts gives (3) azo dyestuffs, cf. (1);  $\bar{C}$  with isatin chloride [Beil. XXI-302, XXI<sub>1</sub>-(296)] yields (5) a chloronaphthalene indolindigo]

[ $\bar{C}$  dislvd. in a little alc., made ammoniacal with conc.  $NH_4OH$ , and treated at 5° with nitrosobenzene in alc. gives (84% yield (8)) 2-chloronaphthoquinone-1,4-monoanil-4 (see under 3:3580), very red ndls. from alc., m.p. 112° (8).

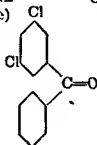
3:1490 (1) Hodgson, Rosenberg, *J. Soc. Chem. Ind.* 48-T, 267-269 (1929). (2) Lesser, Gad, *Ber.* 56, 972-973 (1923). (3) Kalle and Co., *Ger.* 167,458, Jan. 22, 1906; *Cent.* 1906, I 1067. (4) Franzen, Steuble, *J. prakt. Chem.* (2) 103, 383-384 (1921/2). (5) Bedzik, Friedländer, *Monatsh.* 29, 380-381 (1908). (6) Claus, Oehler, *Ber.* 15, 314 (1882). (7) Willstätter, Schuler, *Ber.* 61, 365 Note, 367 (1928). (8) Friedländer, Sander, *Ber.* 57, 646-647 (1924).

# CHAPTER V

## DIVISION A. SOLIDS

(3:1500-3:1999)

3:1505 3,5-DICHLOROBENZOPHENONE  $C_{13}H_5OCl_2$  Beil. S.N. 652  
(3,5-Dichlorophenyl phenyl ketone)



M.P. 65° (1) (2)

Ndls. (from MeOH (1)).

[For prepn. from 3,5-dichloro-4-aminobenzophenone (1) by removal of amino group via diazo reaction see (1); for prepn. from 3,5-dichlorobenzohydrol by oxidn. with  $CrO_3$  (75% yield) see (2).]

$\bar{C}$  fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (2) BzOH (1:0715) and a trace of *m*-dichlorobenzene (3:5900).

③ 3,5-Dichlorobenzophenone oxime: from  $\bar{C}$  in alc. on refluxing 8 hrs. with  $NH_2OH \cdot HCl$  + excess NaOH: after distilling off the alcohol, the mixt. of two stereoisomeric oximes is pptd. by pouring into aq.; sepn. of the two isomers can be effected by fractnl. crystn. from dil. MeOH or dil. EtOH (1).

$\alpha$ -form (less-soluble isomer), pl or fine ndls., m.p. 137°. [With  $PCl_5$  in dry ether, followed by water, this form yields quant. 3,5-dichlorobenzanilide, ndls. from dil. alc., m.p. 148° (1).]

$\beta$ -form (more-soluble isomer), constituting 70% of reaction mixt., pr. m.p. 118°. [With  $PCl_5$  in dry ether, followed by water, this form yields a gummy product from which some benz-3,5-dichloroanilide, ndls. m.p. 148.5°, can be sepd. (1).]

3:1505 (1) Waters, *J. Chem. Soc.* 1929, 2108-2109. (2) Lock, Rödiger, *Ber.* 72, 869-870 (1939).

3:1535 4-CHLORO-3-METHYLPHENOL  $C_7H_7OCl$  Beil. VI - 381  
(4-Chloro-*m*-cresol)



M.P. 66° (1) (11) B.P. 235° (1)  
57° (2) 234-236° (11)  
55.5° (3)

Note that  $\bar{C}$  is often designated in the literature as "p-chloro-m-cresol" or even as "6-chloro-m-cresol"; care must be taken to avoid confusion with the isomeric 6-chloro-3-methylphenol (3:0700).

Odorless cryst. (from lgr.). — Volatile with steam (3).

Both the low-melting and high-melting forms appear to be authentic; whether they are different cryst. forms has never been detd.

[For prepn of  $\bar{C}$  from 2-chloro-5-aminotoluene (4-chloro-3-methylaniline) [Beil. XII-871] via diazo reaction see (3); for comml. prepn. from m-cresol (1:1730) by chlorination with  $SO_2Cl_2$  see (1) (4) (84% yield (11)).]

[ $\bar{C}$  on monobromination with  $Br_2$  in AcOH gives (8) 4-chloro-6-bromo-3-methylphenol, m p. 70.0–70.5° (8);  $\bar{C}$  on dibromination yields (9) 4-chloro-2,6-dibromo-3-methylphenol, m p. 68.5–69.5° (9) (for use of latter in bromometric detn. of  $\bar{C}$  see (10)).]

$\bar{C}$  treated with  $(CH_3)_2SO_4$  + aq. NaOH gives its methyl ether, 4-chloro-3-methylanisole, b p. 213.5° (2). [This methyl ether on oxidn with dil.  $KMnO_4$  (6.7 hrs. for 5 g.) gave (2) 2-chloro-5-methoxybenzoic ac [Beil. X-143], ndls. from dil. AcOH (5), m.p. 173.5° (2), 170–171° (5), Neut. Eq. 186.5.

④ 4-Chloro-3-methylphenyl benzoate: from  $\bar{C}$  +  $BzCl$  + pyridine, pl. from alc., m.p. 86° (2) (3). [This benzoate htd with 0.7 of its wt. of  $AlCl_3$  for 10 min. at 140° gives by Fries rearrangement 100% yield (6) of 2-hydroxy-5-chloro-4-methylbenzophenone, yel. ndls. from dil. alc, m p. 142° (6) ]

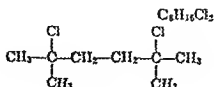
⑤ 4-Chloro-3-methylphenyl benzenesulfonate: from  $\bar{C}$  + benzenesulfonyl chloride + pyridine, pl. from alc., ro p. 66° (3). [Note that this value is numerically the same as orig  $\bar{C}$  and that the deriv must therefore be distinguished from it, e.g., by mixed m p. or behavior with alk.]

⑥ 4-Chloro-3-methylphenyl p-toluenesulfonate: from  $\bar{C}$  + p-toluenesulfonyl chloride + pyridine, pl from alc (2) (3), ndls from lt. pet (2), m.p. 98° (2) (3). [Note that this deriv does not distinguish  $\bar{C}$  from 6-chloro-3-methylphenol (3:0700) or 2-chloro-3-methylphenol (3:1055).]

⑦ 4-Chloro-3-methylphenyl N- $\alpha$ -naphthylcarbamate: from  $\bar{C}$  +  $\alpha$ -naphthyl isocyanate in presence of trace of trimethyl- or triethyl-amine in ether; cryst from lgr., m.p. 153–154° (7).

3:1535 (1) Kalle and Co., Jan 11, 1897, Ger. 90,847, *Friedländer* 4, 94 (1894/7). (2) Gibson, *J. Chem. Soc.* 1926, 1425–1428. (3) Huston, *Chem. J. Am. Chem. Soc.* 55, 4214–4218 (1933). (4) Lasehinger, U.S. 1,847,566, March 1, 1932, *Cent* 1932, II 1512, *C.A.* 26, 2471 (1932). (5) Hodgson, Beard, *J. Chem. Soc* 1926, 164 (6) Rosenmund, Schnurr, *Ann.* 460, 56 (1928). (7) French, Wirtel, *J. Am Chem Soc* 48, 1736–1739 (1926). (8) von Walther, Zipper, *J. prakt. Chem.* (2) 91, 378–379 (1915) (9) Huston, Neeley, *J. Am. Chem. Soc.* 57, 2178 (1935). (10) Desbusses, *Mitt. Lebensm. Hyg* 32, 250–254 (1941); *C.A.* 37, 3023 (1943). (11) Sah, Anderson, *J. Am Chem Soc.* 63, 3165 (1941).

3:1550 2,6-DICHLORO-2,6-DIMETHYLHEXANE  
(Di-isocrotyl-bis-hydrochloride)



Beil. I - 163

I<sub>1</sub>—  
I<sub>2</sub>-(127)

M.P. 66–67° (1)  
64° (2) (3)

Colorless lfts. or ndls., sol. in alc, ether,  $CHCl_3$ , or  $C_6H_6$

[For prepn. of  $\bar{C}$  from 2,5-dimethylhexanediol-2,5 [Beil. I-492, I<sub>1</sub>-(256), I<sub>2</sub>-(557)] with

fumg. HCl (1) or AcCl (1) or in AcOH with HCl gas (100% yield (3)) see (1) (3); from the ring-closed internal ether of the above diol, viz., 2,2,5,5-tetramethyltetrahydrofuran [Beil. XVII-17], with fumg. HCl see (2); for prepn. of  $\bar{C}$  from 2,5-dimethylhexadiene-2,4 (di-isocrotyl) [Beil. I-259, I<sub>1</sub>-(122), I<sub>2</sub>-(237)] with HCl in s.t. see (2).]

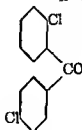
$\bar{C}$  on htg. boils at 180° with evolution of HCl (1).

[ $\bar{C}$  on slow distn. nt 12-20 mm. over CO<sub>2</sub> saturated soda-lime at 255-270° gives (3) by loss of 2 HCl 2,5-dimethylhexadiene-2,4 (see above), m.p. + 6° (2).]

[For study of behavior of  $\bar{C}$  with aq. alc. N/10 NaOH see (4).]

3:1550 (1) Henry, *Compt. rend.* 143, 496-497 (1906). (2) Pogorzelski, *J. Russ. Phys.-Chem. Soc.* 30, 977-992 (1898); *Cent.* 1899, I 773. (3) Staudinger, Muntwyler, Ruzicka, Selbt, *Helv. Chim. Acta* 7, 395-396 (1924). (4) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 9, 1380-1388 (1939); *C.A.* 34, 1611 (1940).

3:1565 2,4'-DICHLOROBENZOPHENONE  
(*o*-Chlorophenyl *p*-chlorophenyl ketone)

C<sub>12</sub>H<sub>8</sub>OCl<sub>2</sub>Beil. VII - 420  
VII<sub>1</sub>—

M.P. 60.5-67.0° (1) (2) B.P. 214-215° at 22 mm. (2)  
66° (3) (4)  
64.2-65.2° cor. (5)

Pr. (from alc.). — [For crystallographic consts. see (3) (4).] — Sol. in most org. solv.; cryst. best from lgr. or cold dil. (60-75%) alc. (2).

[For prepn. from *o*-chlorobenzoyl chloride (3:6640) + chlorobenzene (3:7903) + AlCl<sub>3</sub> in CS<sub>2</sub> see (2); as by-product (besides 4,4'-dichlorobenzophenone (3:4270)) from *p*-chlorobenzoyl chloride (3:6550) + chlorobenzene (3:7903) + AlCl<sub>3</sub> + CS<sub>2</sub> see (3), or from *p*-chlorobenzoic acid (3:4940) + chlorobenzene (3:7903) + AlCl<sub>3</sub> (yield 9-12%) see (1).]

[For formn. of  $\bar{C}$  from 1,1-dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene (3:1925) by oxidn. with CrO<sub>3</sub>/AcOH see (5).]

[ $\bar{C}$  with aq. NaOH + trace CuO in Fe bomb (or in pres. of Fe powder) at 240° for 6 hrs. both ring-closes and hydrolyzes giving (87% yield (6)) crude 3-hydroxyfluorenone, m.p. 184-192° (6).]

⑤ 2,4'-Dichlorobenzophenone 2,4-dinitrophenylhydrazonae: m.p. 230-231° (5).

3:1565 (1) Newton, Groggins, *Ind. Eng. Chem.* 27, 1399 (1935). (2) Norris, Twieg, *Am. Chem. J.* 30, 397 (1903). (3) Montagne, *Rec. trav. chim.* 25, 385-387 (1906). (4) Jaeger, *Z. Krist.* 50, 52 (1921). (5) Haller, Bartlett, Drake, Newman, Cristol, Magerlein, Mueller, Schneider, *J. Am. Chem. Soc.* 67, 1599, 1602 (1945). (6) Britton, Moyle, Bryner (to Dow Chem. Co.), U.S. 2,377,751, June 5, 1945; *C.A.* 39, 4097 (1945).

3:1595 2,6-DICHLOROPHENOL

C<sub>6</sub>H<sub>4</sub>OCl<sub>2</sub>Beil. VI - 190  
VI<sub>1</sub>-(103)  
VI<sub>2</sub>-(179)

M.P. 67° (1) (2) B.P. 219-220° at 740 mm. (2) cf. (3)  
66-68° (8) 80-85° at 4 mm. (2)

Cryst. from pet. eth. with penetrating odor suggesting *o*-chlorophenol or (if dilute) iodoform. — Misc. with alc., ether, volatile with steam.

[For prepn. from *p*-hydroxybenzoic ac (1:0840) by chlorination in AcOH followed by elimin. of CO<sub>2</sub> by htg in quinoline see (4) (5) (8); for prepn. from phenol (1:1420) by prelim. sulfonation, subsequent chlorination in nitrobenzene, and final removal of sulfonic acid group by hydrolysis (70% yield (2)) see (2) ]

$\bar{C}$  is sol. in Na<sub>2</sub>CO<sub>3</sub> soln. (1). [For study of ionization const. see (6).]

$\bar{C}$  on nitration (no details) gives 2,6-dichloro-4-nitrophenol [Beil. VI-241], colorless ndls. from aq., m p. 125° (7)

$\bar{C}$  dislvd. in aq. alk. and shaken with (CH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub> yields (1) (2) the methyl ether, 2,6-dichloroanisole, b.p. 105-106° at 20 mm (2), m p 101° (1).

[For study of rearr. of ethers (8) or esters (9) of  $\bar{C}$  see indic. refs.]

— 2,6-Dichlorophenyl acetate: b p 125-126° at 17 mm.,  $D_{25}^{25} = 1.335$ ,  $n_D^{25} = 1.5281$  (8). [From  $\bar{C}$  with Ac<sub>2</sub>O + pyridine (93% yield (8)).]

⊙ 2,6-Dichlorophenyl benzoate: m p. 74.0-74.5° (9).

— 2,6-Dichlorophenyl *p*-nitrobenzoate: unreported.

— 2,6-Dichlorophenyl 3,5-dinitrobenzoate: unreported.

— 2,6-Dichlorophenyl benzyl ether: m.p. 39.5-40° (10).

— 2,6-Dichlorophenyl *p*-nitrobenzyl ether: unreported.

⊙ 2,6-Dichlorophenoxyacetic acid: ndls from aq., m.p. 134.5-135.0° cor. (9). [From  $\bar{C}$  with chloroacetic acid (3 1370) + aq alk (9) ]

— 2,6-Dichlorophenyl *N*-phenylcarbamate: unreported.

— 2,6-Dichlorophenyl *N*-( $\alpha$ -naphthyl)carbamate: unreported.

— 2,6-Dichlorophenyl *N*-( $\beta$ -naphthyl)carbamate: unreported.

3:1595 (1) Holleman, *Rec trav. chim.* 37, 96-103 (1918). (2) Huston, Neeley, *J. Am. Chem. Soc.* 57, 2177 (1935) (3) Seifart, *Ann. Suppl.* 7, 203 (1870). (4) Richardson, *J. Chem. Soc.* 1937, 1364 (5) Blicke, Smith, Powers, *J. Am. Chem. Soc.* 54, 1468 (1932). (6) Murray, Gordon, *J. Am. Chem. Soc.* 57, 110-111 (1935) (7) Tarugi, *Gazz. chim. ital.* 30, II 490-491 (1900). (8) Tarbell, Wilson, *J. Am. Chem. Soc.* 64, 1068-1069 (1942). (9) Tarbell, Fanta, *J. Am. Chem. Soc.* 65, 2172-2173 (1943) (10) Huston, Eldridge, *J. Am. Chem. Soc.* 53, 2262-2263 (1931).

### 3:1610 8-CHLORONAPHTHOL-1



C<sub>10</sub>H<sub>7</sub>OCl

Beil. VI —

VI<sub>1</sub> —

VI<sub>2</sub>-(582)

M.P. 67° (1)

Ndls. from aq — Volatile with steam.

[For formn. of  $\bar{C}$  from 8-chloro-1-nitronaphthalene [Beil. V-556] by merely refluxing with aq. see (1) ]

$\bar{C}$  is sol. in aq alk. giving orange-colored soln. which couples with solns. of diazonium salts (1).

[For reactn. of  $\bar{C}$  with benzotrichloride (3:6540) yielding 4-benzoyl-8-chloronaphthol-1, m.p 121°, used in prepn. of triphenylmethane dyes see (2); with *o*-nitrophenylsulfenyl chloride see (3); for coupling of  $\bar{C}$  with diazotized 2-hydroxynaphthylamine-1 (or its relatives) yielding *o*-hydroxyazo cpds. see (4) ]

3:1610 (1) Woroshtzow, Koslow, *Ber.* 69, 412-415 (1936). (2) Soc. Chem. Ind. Basel, Ger. 378,908, Aug. 7, 1923. Ger. 378,903, Aug. 11, 1923; Swiss 98,559, April 2, 1923; *Cent.* 1923, IV 594. (3) Akt.-Ges. Anilin-Fabrikation, Ger. 402,642; Sept. 17, 1924; *Cent.* 1924, II 2505. (4) Soc. Chem. Ind. Basel, Brit. 150,433, June 22, 1922; *Cent.* 1922, IV 841.

3:1615  $\alpha$ -CHLOROISOCROTONIC ACID  $\text{CH}_3-\text{C}=\text{C}-\text{H}$   $\text{C}_4\text{H}_5\text{O}_2\text{Cl}$  Beil. II - 415  
 $\text{HOOC}-\text{C}=\text{C}-\text{Cl}$  II<sub>1</sub>-(189)  
 (cis-2-Chlorobuten-2-oic acid-1; allo- $\alpha$ -chlorocrotonic acid) II<sub>2</sub>-(306)

M.P. 67.0-67.5° (1)  
 66-67° (2)  
 67° (3)  
 66.2-66.5° (4) (5)  
 66° (6) (7)

[See also  $\alpha$ -chlorocrotonic acid (3:2760).]

Ndls. from aq. (2) (4) (5); note, however, that from aq. solns. of salts acidification first ppts.  $\bar{C}$  as an oil. —  $\bar{C}$  is more sol. aq. than its stereoisomer; e.g.,  $\bar{C}$  is sol. in 15.3 pts. aq. at 19° (8). —  $\bar{C}$  is much more volatile with steam than its stereoisomer (3:2760) (4) (5). —  $\bar{C}$  is spar. sol. cold but eas. sol. hot lgr. (8).

Preparation. [For prepa. of  $\bar{C}$  from lower-melting form (m.p. 63°) of  $\alpha,\beta$ -dichloro-n-butyric acid (3:1375) with excess 10% aq. NaOH at not above 10° see (4) (5) cf. (9).]

Chemical behavior.  $\bar{C}$  on htg. in s.t. at 150-160° for 12 hrs. (10), or with pyridiae hydrochloride in pyridine 7 days at room temp. or rapidly at 100° (2), or even slowly on steam distillation (11) is converted to the stereoisomeric  $\alpha$ -chlorocrotonic acid (3:2760), m.p. 99°.

$\bar{C}$  on reduction with Na/Hg in aq. is dehalogenated yielding (12) (4) crotonic acid (1:0425), m.p. 72°; whether any isocrotonic acid (1:1045), b.p. 169°, m.p. 15°, is formed at all is uncertain.

$\bar{C}$  with  $\text{Cl}_2$  in  $\text{CS}_2$  adds 1 mole halogen yielding (13) the same  $\alpha,\alpha,\beta$ -trichloro-n-butyric acid (3:1280), m.p. 59.5-60°, also obtd. by like treatment of  $\alpha$ -chlorocrotonic acid (3:2760). — The behavior of  $\bar{C}$  with  $\text{Br}_2$  appears to be unreported.

$\bar{C}$  behaves as a monobasic acid; dissociation const. at 25° is  $1.53 \times 10^{-3}$  (14); Neut. Eq. 120.5.

Salts. [ $\text{K}\bar{\text{A}}$ , ndls. from alc. in which it is much more sol. (viz., 1 pt.  $\text{K}\bar{\text{A}}$  in 22 pts. 99.5% alc. at 16.5° (4)) than its stereoisomer (use in sepn. (2) (9)), eas. sol. aq.;  $\text{Ba}\bar{\text{A}}_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , eas. sol. aq. but spar. sol. alc. (8);  $\text{Pb}\bar{\text{A}}_2 \cdot \text{H}_2\text{O}$ , ppt. (8).]

[For study of rate of reactn. of  $\bar{C}$  with  $\text{K}_3\text{AsO}_3$  see (3).]

The acid chloride of  $\bar{C}$  is unreported.

— Methyl  $\alpha$ -chloroisocrotonate: unreported. [However, for study of rate of esterification of  $\bar{C}$  with MeOH see (15).]

— Ethyl  $\alpha$ -chloroisocrotonate: oil; see 3:9368. [Note also that  $\bar{C}$  in EtOH with conc.  $\text{H}_2\text{SO}_4$  at 100° gives only (7) the stereoisomeric ethyl  $\alpha$ -chlorocrotonate (3:8523).]

—  $\alpha$ -Chloroisocrotonamide: unreported.

—  $\alpha$ -Chloroisocrotonanilide: unreported.

—  $\alpha$ -Chloroisocroton- $\alpha$ -naphthalide: unreported.

3:1615 (1) Stelling, *Z. physik. Chem.* 2, 1008-1010 (1888). (2) Backer, van Oosten, *Rec. trav. chim. É.* (5) Wislicenus, *Ber.* 20, 1008-1010 (1888). (6) Michael, *Ann.* 432, 62 (1923). (7) Michael, *thess. J. prakt. Chem.* (2) 46, 255-258, 4 (1888).

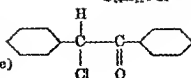
(11) Wislicenus, *Ann.* 248, 337 (1888). (12) Michael, *J. prakt. Chem.* (2) 46, 270-272 (1892). (13) Valentin, *Ber.* 28, 2661-2662 (1895). (14) Ostwald, *Z. physik. Chem.* 3, 244 (1899). (15) Michael, Oechslein, *Ber.* 42, 322 (1909).

3:1618 *d,l*-DESYL CHLORIDE

( $\alpha$ -Chlorodesoxybenzoin,  
*ms*-chlorodesoxybenzoin,  
 $\alpha$ -chlorobenzyl phenyl ketone,  
 $\alpha$ -chloro- $\alpha$ -phenyl-acetophenone)



Beil. VII - 436

VII<sub>1</sub>-(234)

M.P. 68°	(1) cf. (2)
67.5°	(3) (4)
67.0-67.5°	(5)
67°	(6)
66-68°	(7)
66-67°	(8) (9)
66°	(2)
65.5°	(10)
65°	(11) (12)

White cryst. from MeOH, EtOH, lgr., or CHCl<sub>3</sub> by addn. of lt. pet. — Note that on distillation under reduced press.  $\bar{C}$  goes over with only slight decompn. as a green vapor which condenses to a green liquid, on solidification much of this color is lost and recrystallization yields colorless  $\bar{C}$ . —  $\bar{C}$  is quite stable in dark; in sunlight, however, it turns brown and decomposes.

PREPARATION OF  $\bar{C}$ 

[For prepn. of  $\bar{C}$  from benzoin (1:5210) with SOCl<sub>2</sub> in pyridine (yield 74-79% (9)) (5) or with SOCl<sub>2</sub> directly (yield 90% (6)) (2) (3) (10) (13) see indic. refs. — Note that *l*-benzoin with SOCl<sub>2</sub> undergoes racemization (7) yielding  $\bar{C}$ .]

[For formn. of  $\bar{C}$  from  $\alpha,\alpha$ -dichlorobenzyl phenyl ketone (*ms,ms*-dichlorodesoxybenzoin) [Beil. VII-436, VII<sub>1</sub>-(234)] by partial dehalogenative reduction using H<sub>2</sub> + platinum oxide cat. (65% yield (1)) or AcOH + Fe powder at 70-80° (15) see indic. refs.; from 1,2-diphenyl-1,2-epoxyethylene (diphenyloxene) with conc. HCl in s.t. at 120° for 2 hrs. see (11); from benzoyl-phenyl-diazomethane (azibenzil) [Beil. VII<sub>1</sub>-(395)] in ether with HCl gas see (12) ]

CHEMICAL BEHAVIOR OF  $\bar{C}$  WITH INORGANIC REAGENTS

Reduction. [ $\bar{C}$  in alc. solu. with H<sub>2</sub> + platinum oxide cat. (1), or in AcOH with Fe powder on protracted treatment (14), gives benzyl phenyl ketone (desoxybenzoin) (1:5165).]

Oxidation. [ $\bar{C}$  with conc. HNO<sub>3</sub> on warming gives (14) dibenzoyl (benzil) (1:9015).]

Halogenation. [ $\bar{C}$  with Br<sub>2</sub> (1 mole) in AcOH at 100° for ½ hr. gives (10)  $\alpha$ -bromo- $\alpha$ -chlorobenzyl phenyl ketone, m.p. 85° ]

Behavior with alkalis and alkali carbonates. (For alc. alkalies see below under organic reactants ) — [ $\bar{C}$  with powdered KOH (3 moles) in toluene refluxed 2 hrs. loses HCl and rearranges giving (20% yield (11)) 1,2-diphenyl-1,2-epoxyethylene (diphenyloxene), b.p. 174-180° at 18 mm., m.p. 52°; note, however, that two later workers (15) (29) have been unable to duplicate this report. — Note, however, that  $\bar{C}$  with powdered KOH in dry ether gives (15) a mixt. of benzoic acid (1:0715), diphenylacetic acid (1:0765), desoxybenzoin (1:5165), and benzil (1:9015).]

[ $\bar{C}$  with excess ignited Na<sub>2</sub>CO<sub>3</sub> at 200° without solvent for 1 hr. gives (11) a mixt. (yield not stated) of both stereoisomeric 1,2-dibenzoyl-1,2-diphenylethylenes (dibenzoylstilbenes): higher-melting isomer [Beil. VII-844], m.p. 232°; lower-melting isomer [Beil. VII-843, VII<sub>1</sub>-(453)], m.p. 212-214° ]



[ $\bar{C}$  with NaSH in alc. soln. in cold gives (16) benzoyl-phenyl-carbinyl mercaptan (desylthiol), m.p. 42–44° (benzoyl ester, m.p. 110–112° (16)), accompanied by two forms of didesyl sulfide, one of m.p. 168–169°, the other of m.p. 128–129° (16).]

Behavior with metals. [ $\bar{C}$  with Na in  $C_6H_6$  evolves  $H_2$  and on warming gives a mixt. which with aq. followed by dil. acid gives (2) a mixt. of benzoic acid (1:0715) + benzoic acid (1:0770) together with an unidentified neutral oil.]

Behavior with other inorganic reactants. [ $\bar{C}$  with moist silver oxide in ethylene glycol at 100° for 3 hrs., then boiled 2 hrs., gives (29) 1,2-dibenzoyl-1,2-diphenylethane (bidesyl) [Beil. VII-841, VII<sub>1</sub>-(452)], m.p. 254–255° (29).]

## CHEMICAL BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

Behavior with arom. hydrocarbons +  $AlCl_3$ . [ $\bar{C}$  with  $C_6H_6$  (1:7400) +  $AlCl_3$  gives (78% yield (17)) (18) (19)  $\omega,\omega$ -diphenylacetophenone (*ms*-phenyldeoxybenzoin = triphenylvinyl alc.). [Beil. VII-522, VII<sub>1</sub>-(291)], m.p. 137° (19), 135–136° (17) (18). —  $\bar{C}$  with toluene (1:7405) +  $AlCl_3$  gives (77% yield (17))  $\omega$ -phenyl- $\omega$ -(*p*-tolyl)acetophenone ( $\alpha$ -(*p*-tolyl)-desoxybenzoin), m.p. 97–98° (17). —  $\bar{C}$  with mesitylene (1:7455) +  $AlCl_3$  in  $CS_2$  gives (13)  $\omega$ -phenyl- $\omega$ -mesitylacacetophenone ( $\alpha$ -mesityldeoxybenzoin), m.p. 111–112° (13).] (See also below under reactn. of  $\bar{C}$  with  $RMgX$  cpds.)

Behavior with organic hydroxy or mercapto compounds. With alcohols (or alkoxides). [ $\bar{C}$  in MeOH with MeOH/NaOMe gives (80% yield (11)) 1,2-diphenyl-1-methoxy-1,2-epoxyethane, h.p. 194–196° at 16 mm., accompanied by some *cis* + *trans* dibenzoylstilbene (see above).]

[ $\bar{C}$  in EtOH with EtOH/NaOEt gives similarly a prod., h.p. 188° at 12 mm., regarded (11) as 1,2-diphenyl-1-ethoxy-1,2-epoxypropane. — Note, however, that  $\bar{C}$  in EtOH/NaOEt or with alc. NaOH at 25° gives (5) cf. (1) benzoin (1:5210) and that under certain conditions an apparently intermediate benzoin diethylacetal  $C_6H_5CH(OH).C(OC_2H_5)_2.C_6H_5$ , m.p. 66–67°, can be isolated (5).]

With phenols (or alkali phenates). [ $\bar{C}$  with phenol + anhydrous  $K_2CO_3$  in acetone refluxed 5 hrs. (20) or  $\bar{C}$  with Na phenate (21) gives (59% yield (20)) desyl phenyl ether (the phenyl ether of benzoin), m.p. 85.5° (21), 85° (20); note that this prod. is isomeric with, but different from, *ms*-phenylbenzoin [Beil. VIII-211], whose m.p. is almost the same; note also that desyl phenyl ether on attempted distillation at ord. press. undergoes a fission into phenol and a cpd. regarded (21) as 2,2,4,4-tetraphenylcyclobutanedione-1,3, m.p. 244–245°.]

With mercaptans. [ $\bar{C}$  +  $\alpha$ -mercaptoacetic acid (thioglycolic acid) at 100° for 6 hrs. evolves  $HCl$  and yields (22) *S*-desylthioglycolic acid, m.p. 105° (corresp. oxime, m.p. 123°; corresp. semicarbazone, m.p. 178° (22)). —  $\bar{C}$  with  $\beta$ -mercapto propionic acid at 100° for 6 hrs. evolves  $HCl$  and yields (16)  $\beta$ -(desylthio)propionic acid, m.p. 108–109°.]

[ $\bar{C}$  with thiophenol in EtOH/NaOEt gives in good yield (16) desyl phenyl sulfide, m.p. 83–84° (16), 81° (23). —  $\bar{C}$  in MeOH with aq. sodium thiosalicylate gives (22) *S*-desylthiosalicylic acid, m.p. 189°.]

Behavior with carbonyl compounds. [For behavior of  $\bar{C}$  with cyclohexanone + sodium in di-*n*-butyl ether see (24).]

Behavior with organic acids (or their salts). [ $\bar{C}$  with anhydrous NaOAc in excess  $Ac_2O$  refluxed 1 hr. yields (11) mainly the  $\beta$ -stereoisomer, m.p. 153°, of 1,2-diacetoxy-1,2-diphenylethylene [Beil. VI-1026, VI<sub>1</sub>-(499)], accompanied by some of the more sol.  $\alpha$ -stereoisomer, m.p. 118°.]

[ $\bar{C}$  +  $K$  thiobenzoate in abs. alc. boiled 10 min. gives (100% yield (16)) desyl thiobenzoate, m.p. 110–112°.]

[ $\bar{C}$  in aq. alc. KCN does not directly eliminate  $KCl$  and give the corresp. desyl cyanide

(*ms*-cyanodesoxybenzoin) [Beil. X-755, X<sub>1</sub>-(360)] which might be expected although this compd., m p. 90-92° (25), 89-90° (26), is well known and preparable (yields 60% (25), 47% (26)) from benzyl cyanide + ethyl benzoate and otherwise. — Instead  $\bar{C}$  in aq. alc. KCN loses HCl and gives (27) (28) 1-cyano-1,2-diphenyl-1,2-epoxyethane ( $\alpha$ -cyano- $\alpha,\beta$ -diphenyl-ethylene oxide) which obviously can exist in two geometrically stereoisomeric forms: one has m p. 74° (27), 77-78° (28); the other has m.p. 52° (27); for much further detail especially with reference to further reactn prods of these epoxynitriles see (27) (28) ]

Behavior of  $\bar{C}$  with RMgBr reactants. (See also above under behavior of  $\bar{C}$  with hydrocarbons + AlCl<sub>3</sub>.)

[ $\bar{C}$  with C<sub>6</sub>H<sub>5</sub>MgBr (2 moles) gives (29) (21) the prod. normally to be expected, viz., 1,1,2,2-tetraphenylethanol-1 [Beil. VI-732, VI<sub>1</sub>-(364)], m p. 236° (21) (30), 230.5° (29); the intermediate ketone, viz., *ms*-phenyldesoxybenzoin (for consts. see above reference) may sometimes (21) be formed, but for discussion of possible alternative mechanisms see (21) (29) ]

$\bar{C}$  with the three tolyl MgBr reactants has been studied, but the reaction is complex and shows no tendency to go way through to the expected tetraarylethanol (only one of which has been reported by any means). — [ $\bar{C}$  with *o*-tolyl MgBr (2 moles) gives (29) a mixt. of prods., including the expected intermediate ketone, viz., *ms*-(*o*-tolyl)desoxybenzoin, m p. 56-57° (32); note, however, that the 1,2-diphenyl-1,2-di-(*o*-tolyl)ethanol-1 which should be the end prod. is unknown. —  $\bar{C}$  with *m*-tolyl MgBr gives (29) similarly a mixt. of prods. including the intermediate ketone, viz., *ms*-(*m*-tolyl)desoxybenzoin, m.p. 83-84° (32), 82.5-83.5° (29), 82-83° (33), but again the ultimate 1,2-diphenyl-1,2-di-(*m*-tolyl)-ethanol-1 is unknown. —  $\bar{C}$  with *p*-tolyl MgBr (2 moles) gives (31) the ketone *ms*-(*p*-tolyl)desoxybenzoin, m.p. 97-98° (17), 96-97° (31); the ultimate 1,1-diphenyl-1,2-di-(*p*-tolyl)ethanol-1, m.p. 195-196°, has been obtd. by other means (29) ]

Behavior of  $\bar{C}$  with amines. With primary amines [ $\bar{C}$  (1 mole) with aniline (2 moles) in alc. at room temp. for 24 hrs gives (6) *N*-(desyl)aniline (benzoin anil = *ms*-anilindesoxybenzoin) [Beil. XIV-103, XIV<sub>1</sub>-(395)], m p. 99°; note that  $\bar{C}$  with aniline at 140-150° for 1 hr. (34) ppt. aniline hydrochloride and leaves a mixt. contg. benzoin-anil = anilide (cf. (35)) since with benzaldehyde at 150-160° for 1 hr. under CO<sub>2</sub> it yields pentaphenyldihydroimidazole (34) —  $\bar{C}$  with *p*-toluidine in alc. at room temp. for 24 hrs gives (3) similarly *N*-(desyl)-*p*-toluidine (*ms*-(*p*-toluidine)desoxybenzoin), m.p. 145° ]

[For corresp. reactns. of  $\bar{C}$  with *m*-chloroaniline, *p*-chloroaniline, *m*-bromoaniline, *p*-iodoaniline, *p*-aminophenol, *p*-phenetidine, *p*-aminoacetanilide, or ethyl *p*-aminobenzoate see (3), for study of rate of this group of reactns. see (4); note that *o*-toluidine, *o*-chloroaniline, and *o*-anisidine do not undergo this reactn. (3).]

With secondary amines. [ $\bar{C}$  with Me<sub>2</sub>NH (2-3 moles) in alc. in s.t. at 100-110° gives (36) *ms*-(dimethylamino)desoxybenzoin, m.p. 59-61° (36).]

[ $\bar{C}$  (1 mole) with *N*-methylaniline (2 moles) in alc. refluxed 2½ hrs. gives (47% yield (3)) *ms*-(*N*-methyl-*N*-phenylamino)desoxybenzoin, m.p. 100°; if reactants in alc. are stood at room temp. for 100 days, yield is 61% (3).]

[ $\bar{C}$  with piperidine at 100° for 20 min. gives (8) *ms*-(piperidino)desoxybenzoin [Beil. XXI-(14)], m p. 85-86° (3).]

With phenylhydrazine  $\bar{C}$  (1 mole) with phenylhydrazine (2 moles) in abs. alc. at room temp. for 3 days ppt. phenylhydrazine hydrochloride and yields (37) benzil bis-(phenylhydrazone) = benzil-phenyllosazone, m.p. 233° dec. (37) [cf. under benzil (1:9015)]

⑦ *N*-Desylphthalimide [Beil. XXI-480, XXI<sub>1</sub>-(374)]: pale yel. cryst. from AcOH. m p. 157-158° (38), 155-156° (39). [From  $\bar{C}$  with K phthalimide at 100° for 2 hrs. (24% yield (39)); note that  $\bar{C}$  + potassium phthalimide in nitrobenzene at 150-160°

for 1½ hrs. gives a mixt. of *N*-desylphthalimide with the lower-melting stereoisomer of dibenzoylstilbene (1,2-dibenzoyl-1,2-diphenylethylene) [Beil. VII-843, VII-(453)], m.p. 208° (39) (see also above).]

- 3:1618 (1) Buck, Ide, *J. Am. Chem. Soc.* **54**, 4363 (1932). (2) Schroeter, Caspar, *Ber.* **42**, 2348-2349 (1909). (3) Cameron, Nixon, Basterfield, *Trans. Roy. Soc. Canada* (3) **25**, III 145-156 (1931); *Cent.* 1932, I 2032; *C.A.* **26**, 3250 (1932). (4) Cameron, Nixon, Basterfield, *Trans. Roy. Soc. Canada* (3) **25**, III 157-169 (1931); *Cent.* 1932, I 2033; *C.A.* **26**, 3251 (1932). (5) Ward, *J. Chem. Soc.* 1929, 1541-1553. (6) Cameron, *Trans. Roy. Soc. Canada* (3) **23**, III 53-60 (1929); *Cent.* 1930, I 1133; *C.A.* **24**, 610 (1930). (7) McKenzie, Wren, *J. Chem. Soc.* **97**, 481-482 (1910). (8) Henley, Turner, *J. Chem. Soc.* 1931, 1185. (9) Ward, *Org. Syntheses*, Coll. Vol. 2 (1st ed.) 159-160 (1943); **12**, 20-21 (1932). (10) Taylor, Forsey, *J. Chem. Soc.* 1930, 2276. (11) Madelung, Oberwegner, *Ann.* **194**, 224-234 (1931). (12) Curtius, Lang, *J. prakt. Chem.* (2) **44**, 548-549 (1891). (13) Maxwell, Adams, *J. Am. Chem. Soc.* **52**, 2970 (1930). (14) Lachowicz, *Ber.* **17**, 1163 (1884). (15) Richard, *Compt. rend.* **197**, 1432-1434 (1933). (16) Schönberg, Iskander, *J. Chem. Soc.* 1942, 93-94. (17) Koelsch, *J. Am. Chem. Soc.* **54**, 2031 (1932). (18) Richard, *Compt. rend.* **200**, 754 (1935). (19) Anschütz, Förster, *Ann.* **363**, 93-94 (1909). (20) Bradsher, Rosher, *J. Am. Chem. Soc.* **61**, 1525 (1939). (21) Richard, *Compt. rend.* **198**, 1242-1244 (1934). (22) Behaghel, Schneider, *Ber.* **68**, 1590, 1593 (1935). (23) Mitchell, Smiles, *J. Chem. Soc.* 1933, 1529. (24) Allen, *Can. J. Research* **4**, 271-272 (1931). (25) Kohler, Blatt, *J. Am. Chem. Soc.* **50**, 507-508 (1928). (26) Howk, McElvain, *J. Am. Chem. Soc.* **54**, 286 (1932). (27) Kohler, Brown, *J. Am. Chem. Soc.* **55**, 4299-4304 (1933). (28) Richard, *Compt. rend.* **193**, 943-945 (1934). (29) Roger, McGregor, *J. Chem. Soc.* 1934, 1850-1853. (30) Wegler, *Ber.* **67**, 35-39 (1934). (31) McKenzie, Roger, McKay, *J. Chem. Soc.* 1932, 2603. (32) Roger, McKay, *J. Chem. Soc.* 1933, 336. (33) Roger, McGregor, *J. Chem. Soc.* 1932, 443. (34) Langenbeck, Hotschenreuter, Jöttemann, *Ann.* **485**, 54, 57-58 (1931). (35) Strain, *J. Am. Chem. Soc.* **50**, 2221 (1928). (36) Thomson, Stevens, *J. Chem. Soc.* 1932, 1937. (37) Bodfors, *Ber.* **71**, 481 (1939). (38) Neumann, *Ber.* **23**, 995 (1890). (39) McKenzie, Barrow, *J. Chem. Soc.* 1933, 1333 (1913).

## 3:1620 2,4,5-TRICHLOROPHENOL

C<sub>6</sub>H<sub>3</sub>OCl<sub>3</sub>Beil. VI —  
VI—  
VI—(180)

M.P. 68°	(1) (2)	B.P. 244-248° at 746 mm.	(5) (9)
67.5°	(3)		
66-67°	(4)		
66°	(3) (6) (7)		
64-65°	(8)		
63°	(9)		

Colorless ndls. from alc. or lgr. — Volatile with steam. — Sublimes.

[For prepn. of  $\bar{C}$  from 1,2,4,5-tetrachlorobenzene (3:4115) with MeOH/NaOH in s.t. at 160° for 7 hrs. (yields: 85% (5), 80% (10)) (note that by this method  $\bar{C}$  is sometimes sole product (5), at others is accompanied (7) (10) by some of its methyl ether (2,4,5-trichloroanisole) (see below)) see indic. refs.; from 2,4,5-trichloroaniline via diazotization in conc. H<sub>2</sub>SO<sub>4</sub> as directed followed by htg. at 170-180° (65% yield (9)) see indic. refs.; from 2,4,5-trichloro-1-fluorobenzene with NaOMe see (6); from 3,5,6-trichloro-2-hydroxybenzoic acid by htg. with soda-lime at 185° see (3); from 2,4-dichloro-5-aminophenyl *o*-amino-*p*-toluenesulfonate via diazotization, use of Cu<sub>2</sub>Cl<sub>2</sub> reactn., and subsequent hydrolysis as directed see (4); from 2,5-dichlorophenol (3:1190) with Cl<sub>2</sub> in AcOH (9) or in AcOH + NaOAc (4) see indic. refs.]

$\bar{C}$  behaves as a weak monobasic acid (ioniz. const. at 25° =  $4.3 \times 10^{-8}$  (2)) but can be titrated with *N*/10 nq. NaOH; Neut. Eq. calcd. 197.5, found 197.1 (1). —  $\bar{C}$  forms a spar.

sol. K salt (4). —  $\bar{C}$  in toluene treated with MeOH/NaOH yields (11) anhydrous Na salt; from aq. this prod. cryst. as pentahydrate (12). — [For prepn. of Na, K, or Li salts see (12), of Ca or Ba salts see (13), of Zn salt see (14). — For use of these salts as fungicides see (11) (12) (13) (14) (15); for use of  $\bar{C}$  with triphenyl phosphate as wood preservative see (16).]

$\bar{C}$  with Br<sub>2</sub> in AcOH (9) or with excess Br<sub>2</sub>/aq (17) yields 6-bromo-2,4,5-trichlorophenol, cryst. from AcOH or lt. pet., m.p. 81–82° (17), 81° (9) (corresp. benzoate, m.p. 116–117° (9)). —  $\bar{C}$  with Br<sub>2</sub> in pres. of Fe powder yields (9) 3,6-dibromo-2,4,5-trichlorophenol, ndls. from AcOH, m.p. 195° (9) (corresp. benzoate, m.p. 176° (9)).

$\bar{C}$  treated below 10° with conc. HNO<sub>3</sub> (*D* = 1.43) in AcOH gives (90% yield (5)) 6-nitro-2,4,5-trichlorophenol, pale yel. lts. from lgr., m.p. 92–93° (5), 81° (9).

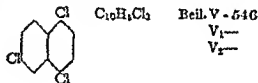
$\bar{C}$  dislvd. in 20% NaOH refluxed with Me<sub>2</sub>SO<sub>4</sub> gives (78.5% yield (5)) (9) corresp. methyl ether (2,4,5-trichloroanisole), ndls. from alc., m.p. 75° (5), 77.5° (9).

⑥ 2,4,5-Trichlorophenyl benzoate: ndls. from alc., m.p. 92–93° (9), 91–92° (4), 89–90° (3). [From  $\bar{C}$  in dil. alk. by shaking with benzoyl chloride (9).]

⑦ 2,4,5-Trichlorophenoxyacetic acid: m.p. 153° (see 3:4335).

3:1620 (1) Tiessens, *Rec. trav. chim.* 50, 114 (1931). (2) Tiessens, *Rec. trav. chim.* 48, 1068 (1929). (3) Farinhardt, Stuart, Twiss, *J. Am. Chem. Soc.* 62, 1240 (1940). (4) Groves, Turner, Sharp, *J. Chem. Soc.* 1929, 516–517. (5) Harrison, Peters, Rowe, *J. Chem. Soc.* 1943, 235–237. (6) de Crauw, *Rec. trav. chim.* 48, 1064–1065 (1929). (7) Holleman, *Rec. trav. chim.* 39, 736–738 (1929). (8) A.G.F.A., Ger. 349,794, March 9, 1922, *Cent.* 1922, IV 45 (9) Kohn, Fink, *Monatsh.* 58, 83–86 (1931). (10) A.G.F.A., Ger. 411,052, March 23, 1925, *Cent.* 1925, I 2411. (11) Mills (to Dow Chem. Co.), U.S. 1,955,089, April 17, 1934, *Cent.* 1934, II 1991. (12) Mills (to Dow Chem. Co.), U.S. 2,039,434, May 5, 1939, *Cent.* 1937, I 984. (14) Mills (to Dow Chem. Co.), U.S. 1,094,002, March 12, 1935, *Cent.* 1935, II 2431. (15) Ellis (to Insulite Co.), U.S. 2,191,654, June 6, 1939, *Cent.* 1939, II 4620. (16) Norton (to Dow Chem. Co.), U.S. 2,304,013, Dec. 1, 1942, *C.A.* 37, 2908 (1913). (17) Fox, Turner, *J. Chem. Soc.* 1930, 1863.

### 3:1625 1,4,6-TRICHLORONAPHTHALENE



M.P. 69° (4)

68° (1)

65° (2) (3) (5) (7)

58° (1)

56° (2) (3) (7) (8) see text

Ndls. from alc.; spar. sol. boilg. alc. (2). — Volatile with steam. — Sublimes.

$\bar{C}$  shows the double m.p. phenomena also exhibited by several of its isomers; if the fused  $\bar{C}$  in a m.p. tube is allowed to cool and then withdrawn from the bath it soon solidifies to a translucent mass which upon immediate reimmersion melts at 58°, but if left for a short time in the air it becomes opaque and then shows m.p. 68°; the translucent form rarely persists more than 20 min. (1).

[For prepn. of  $\bar{C}$  from 5,8-dichloronaphthylamine-2 [Beil. XII-1310] via diazotization and use of Cu<sub>2</sub>Cl<sub>2</sub> reactn. see (4); for prepn. of  $\bar{C}$  from 1,6-dichloro-4-nitronaphthalene [Beil. V-556] (5) (2), from 4,6-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-162] (6), from 4,7-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-163] (7), from 1,4-dichloronaphthalenesulfonyl chloride-7 [Beil. XI-183] (8) (6), from 1-chloro-4-nitronaphthalene-

$\bar{C}$  is readily nitrated; e.g.,  $\bar{C}$  (16 g.) dislvd. in a soln. of  $\text{NaNO}_3$  (12 g.) in aq. (180 ml.), treated during 1 hr. at 90–100° by grad. addn. of dil.  $\text{H}_2\text{SO}_4$  (1:5; 48 ml.), htd. 2 hrs. then steam-distd., gave (3) in distillate 3,5-dichloro-2-nitrophenol (5 g.), lemon-yel. ndls. from pet. ether m.p. 51°, and by repeated hot dil.  $\text{HCl}$  extraction of tarry residue 3,5-dichloro-4-nitrophenol (6 g.) pale yel. ndls. from aq., m.p. 150° (3). [This latter product also results from the action of nitrous acid (3).]

$\bar{C}$  dislvd. in 4 pts.  $\text{AcOH}$  and treated with 3 pts. fuming  $\text{HNO}_3$  for  $\frac{3}{4}$  hr. at 70° (2) gives (60% yield (2)) of 3,5-dichloro-2,4,6-trinitrophenol, pale yel. pr. from  $\text{AcOH}$ , m.p. 139–140° cor. (2).

$\bar{C}$  dislvd. in 5 pts.  $\text{AcOH}$  gives with  $\text{Br}_2$  (as specified (4)) 100% yield of 3,5-dichloro-2,4,6-tribromophenol, cryst. from  $\text{AcOH}$ , m.p. 183° (4).

$\bar{C}$  dislvd. in aq.  $\text{NaOH}$  and shaken with  $(\text{CH}_3)_2\text{SO}_4$  gives the methyl ether, 3,5-dichloro-anisole, m.p. 39° (6). [The value of 65° given in Ref. 6, p. 104, is probably erroneous.]

Ⓔ 3,5-Dichlorophenyl acetate: m.p. 38° (5).

Ⓕ 3,5-Dichlorophenyl benzoate: m.p. 55° (5).

3:1670 (1) Blanksma, *Rec. trav. chim.* 27, 29–30 (1908). (2) Willstätter, Schudel, *Ber.* 51, 784–787 (1918). (3) Hodgson, Wignall, *J. Chem. Soc.* 1927, 2217–2218. (4) Kohn, Pfeifer, *Monatsh.* 48, 237–239 (1927). (5) Hodgson, Wignall, *J. Chem. Soc.* 1926, 2077–2079. (6) Holleman, *Rec. trav. chim.* 37, 103–107, 201 (1918). (7) Murray, Gordon, *J. Am. Chem. Soc.* 57, 110–111 (1935).

### 3:1673 2,4,6-TRICHLOROPHENOL


 $\text{C}_6\text{H}_3\text{OCl}_3$ 

Beil. VI - 190

 VI<sub>1</sub>-(103)

 VI<sub>2</sub>-(181)

M.P. 69.5°	(1)	B.P. 246°	at 760 mm. (1)
69° u.c.	(2)	245°	(8)
69°	(3) (4)	243.5–244.5°	(12)
68°	(5) (6) (7) (8)	242–246°	at 748 mm. (9)
67–68°	(9) (10) (11)		
	(12) (23)		
67.0°	(13)		
67°	(14)		
66.7°	(15)		
66–67° cor.	(16)		

Colorless cryst. from lgr. — Ndl. with 1 mole solvate from  $\text{AcOH}$ , latter lost over  $\text{CaO}$  (17).

$\bar{C}$  is almost insol. aq.: 1000 g. aq. at 11.2° dis. 0.51 g.  $\bar{C}$  (14); at 25.4°, 0.858 g.  $\bar{C}$  (14); at 96°, 2.43 g.  $\bar{C}$  (14). —  $\bar{C}$  is volatile with steam, but not from alk. soln. (difference and sepn. from o-chlorophenol (3:5980) or p-chlorophenol (3:0475) (18)). —  $\bar{C}$  is eas. sol. alc. or ether.

Binary systems contg.  $\bar{C}$ . —  $\bar{C}$  + nitrobenzene: this system forms a 1:1 molecular compound, m.p. 31°; this compd. forms with  $\bar{C}$  a eutectic, m.p. 28.7° contg. 65 wt. %  $\bar{C}$ , and with nitrobenzene a eutectic, m.p. + 2.0° contg. 15.5 wt. %  $\bar{C}$ ; for data and f.p./compn. diagram see (13). —  $\bar{C}$  + diphenylamine: for partial f.p./compn. data and diag. see (19). —  $\bar{C}$  + 2,4,6-tribromophenol: for f.p./compn. data and diag. see (20). —  $\bar{C}$  +  $\alpha,\alpha,\alpha,\alpha'$ -tetramethylphthalan: for study of this system see (15). —  $\bar{C}$  + 2,4,6-trinitroresorcinol (styphnic acid): forms no mol. cpd. but gives a eutectic, m.p. 60° contg. 91.8%  $\bar{C}$  (21).

PREPARATION OF  $\bar{C}$ 

From phenol. *By direct action of chlorine.* [For prepn. of  $\bar{C}$  from phenol (1:1420) with  $Cl_2$  see (3) (for very old initial work cf. (22) (12)); with  $Cl_2$  + aq. alk. (i.e., with  $NaOCl$ ) see (23) (16) (24)]

*By indirect action of chlorine.* [For prepn. of  $\bar{C}$  from phenol (1:1420) by chlorination with ethyl *N,N*-dichlorocarbamate (25), with *N,N'*-dichlorourea (26), with conc.  $HCl$  + 30%  $H_2O_2$  (27), or with  $HCl$  +  $KClO_3$  (28) (29) see indic. refs.]

From other phenols or their relatives. [For formn. of  $\bar{C}$  from 2,4,6-trichloro-3-hydroxybenzaldehyde (6) by elimination of the aldehyde group with 50% aq.  $KOH$  at 60-70° for 4 hrs. (89.9% yield) see (6); from 2,4,6-trichloro-3-bromophenol (see below) or from 2,4,6-trichloro-3,5-dibromophenol (see below) by replacement of  $Br$  by  $H$  through use of  $Zn$  +  $AcOH$  see (9); from 2,4,6-tribromophenol [Beil. VI-203, VI-1(107)] by replacement of all bromine by chlorine using  $Cl_2$  in  $AcOH$  see (30).]

[For formn. of  $\bar{C}$  from phenol-*p*-sulfonic acid [Beil. XI-241, XI-1(55)] (10) or its alkali salts (31) (32) in aq. soln. with  $Cl_2$  (100% yield (10)) see indic. refs.; from aq. *p*-hydroxyazobenzene [Beil. XVI-96, XVI-1(233)] (75% yield (11)), from benzyl phenyl ether [Beil. VI-432, VI-1(220)] (33), from *o*-hydroxybenzyl alcohol (saligenin) (1:1490) (34) with  $Cl_2$  see indic. refs.; from dipotassium salt of salicylic acid (1:6780) with aq.  $KOCl$  (4 moles) see (8).]

From other miscellaneous sources. [For formn. of  $\bar{C}$  from aniline in  $HCl$  soln. with  $Cl_2$  see (35); from 2,4,6-trichloroaniline via diazotization and subsequent hydrolysis as directed see (7); from indigo [Beil. XXIV-417, XXIV-1(370)] in aq. suspension with  $Cl_2$  see (36) (37); from benzene (1:7400) with  $Cl_2O$  see (38); from 2,4,6-trichlorophenyl hypochlorite (see below) by warming with acids or alkalis see (75).]

USES OF  $\bar{C}$  (OR ITS SALTS)

Although the topic cannot here be exhaustively pursued, the bactericidal, fungicidal, and general antiseptic action of  $\bar{C}$  or its salts has attracted much attention [for examples of useful articles in this general connection, see (39) (40) (41) (42) (43) (44) (45) (46); for patents on use of  $\bar{C}$  or its salts in the indicated fields see the following: for use of  $\bar{C}$  (with triaryl phosphates) as wood preservative (47), as preservative for glue (48), as insecticide and fungicide for board-like compns. from vegetable fibers (49), as bactericide (50) (51), as  $Na\bar{A}$  for anti-mildew treatment of textiles (52), as textile asst. in mercerization (53); for various complexes contg.  $\bar{C}$  and intended for use as insecticides, etc., see (54) (55) (56)].

CHEMICAL BEHAVIOR OF  $\bar{C}$ 

Reduction of  $\bar{C}$ . [The catalytic hydrogenation of  $\bar{C}$  apparently has not been extensively studied, but it is said (57) to be more stable toward  $H_2$  +  $PdCl_2$  than the corresponding 2,4,6-tribromophenol.]

Oxidation of  $\bar{C}$ .  $\bar{C}$  on oxidn. gives various products according to circumstances [e.g.,  $\bar{C}$  in 2 *N*  $H_2SO_4$  on electrolytic oxidn. gives (58) 2,6-dichlorohydroquinone (3:4600);  $\bar{C}$  on oxidn. with  $CrO_3/AcOH$  (59) (60) (61) (62) (63), with cold fuming  $HNO_3$  (12) (63), with  $HNO_3/H_2SO_4$  (64), with  $NO$  +  $NO_2$  in alc. (65) (66) or  $AcOH$  (61), or with  $PbO_2$  in  $AcOH$  or  $C_4H_6$  (61) gives (yields: 69% (59), 45% (60), 27% (61)) 2,6-dichlorobenzoquinone-1,4 (3:3750) (note that this product may be accompanied (61) by more or less 2-chloro-6-(2',4',6'-trichlorophenoxy)benzoquinone-1,4, m.p. 131-135°, and 2,6-bis-(2',4',6'-trichlorophenoxy)benzoquinone-1,4, m.p. 245°, which resemble the main prod. in appearance, composition, and behavior (61))].

[ $\bar{C}$  on oxidn. with boilg. mixt. of conc.  $\text{HNO}_3 + \text{HCl}$  gives (16) 2,3,5-trichlorobenzoquinone-1,4 (3:4672).]

[ $\bar{C}$  on oxidn. with  $\text{ClSO}_3\text{H}$  (67), with  $\text{Cl}_2 + \text{fumg. H}_2\text{SO}_4$  followed by  $\text{ClSO}_3\text{H}$  (68), with aqua regia (69) (70) (72), with  $\text{HCl} + \text{KClO}_2$  (28) (16), with  $\text{CrO}_3/\text{AcOH}$  (71) or  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$  (71) gives (90% yield (68)) 2,3,5,6-tetrachlorobenzoquinone-1,4 (chloranil) (3:4978).]

[For study of oxidn. potential of  $\bar{C}$  see (73).]

Nuclear substitution of  $\bar{C}$ . *Chlorination*. [ $\bar{C}$  in  $\text{HCl}$  suspension with  $\text{Cl}_2$  (74) or in  $\text{AcOH}$  soln. with  $\text{Ca}(\text{OCl})_2$  (75) gives 2,4,6-trichlorophenyl hypochlorite (2,4,4,6-tetrachlorocyclohexadien-2,5-one-1) [Beil. VII-147, VII<sub>1</sub>-(96)], scales from ether/pet. ether, m.p.  $122^\circ$  (75) (10),  $121$ – $122^\circ$  (76),  $119^\circ$  (74).]

[ $\bar{C}$  with  $\text{Cl}_2 + \text{ShCl}_3$  at not above  $130^\circ$  gives (77) 2,3,4,4,5,6-hexachlorocyclohexadien-2,5-one-1 ("hexachlorophenol") (3:3180), m.p.  $107^\circ$ .]

[ $\bar{C}$  with  $\text{Cl}_2$  (3) in pres. of  $\text{I}_2$  at  $40^\circ$  (78), or  $\bar{C}$  with  $\text{Cl}_2$  in  $\text{CCl}_4$  in pres. of  $\text{FeCl}_3$  (79), or  $\bar{C}$  with  $\text{Cl}_2$  in pres. of  $\text{ShCl}_3$ ,  $\text{I}_2$ , or  $\text{FeCl}_3$  at  $70$ – $75^\circ$  (80), gives 2,3,4,6-tetrachlorophenol (3:1687), m.p.  $69^\circ$ .]

[ $\bar{C}$  with  $\text{Cl}_2$  in pres. of  $\text{ShCl}_3$ ,  $\text{I}_2$ , or  $\text{FeCl}_3$  at  $135$ – $140^\circ$  gives (81) pentachlorophenol (3:4850), m.p.  $190^\circ$ .]

[ $\bar{C}$  with  $\text{FeCl}_3$  (no details) yields (14) 1,2,3,5-tetrachlorobenzene (3:0915), m.p.  $51^\circ$ .]

*Bromination*. [ $\bar{C}$  with  $\text{Br}_2/\text{aq. KBr}$  soln. as directed (82) (83) gives a monobromo derivative of  $\bar{C}$  frequently designated as "trichlorophenol bromide"; which of the three structures 4-bromo-2,4,6-trichlorocyclohexadien-2,5-one-1, 2-bromo-2,4,6-trichlorocyclohexadien-2,5-one-1, or 2,4,6-trichlorophenyl hypobromite should be assigned to this prod. has never been decisively settled (83); however, on oxidn. with fumg.  $\text{HNO}_3$  it gives (82) 2,6-dichlorobenzoquinone-1,4 (3:3750) and with conc.  $\text{H}_2\text{SO}_4$  at  $100^\circ$  isomerizes (82) to 3-bromo-2,4,6-trichlorophenol, m.p.  $73^\circ$  (9) (corresp. benzoate, m.p.  $117^\circ$  (82)).]

[ $\bar{C}$  with  $\text{Br}_2$  (large excess) +  $\text{Fe}$  powder at room temp. for 24 hrs. gives (100% yield (84)) cf. (85) 3,5-dibromo-2,4,6-trichlorophenol, cryst. from  $\text{AcOH}$ , m.p.  $204^\circ$  cor. (corresp. methyl ether, m.p.  $127^\circ$ ; corresp. benzoate, m.p.  $196^\circ$  (84)).]

*Nitration*. [The direct nitration of  $\bar{C}$  has not been reported, presumably because nitration reagents readily oxidize free  $\bar{C}$  to 2,6-dichlorobenzoquinone-1,4 (3:3750) (see above under oxidn. of  $\bar{C}$ ). — However, both possible nitration products have been obtained by indirect means: for 3-nitro-2,4,6-trichlorophenol, m.p.  $71$ – $72^\circ$ , see (86); for 3,5-dinitro-2,4,6-trichlorophenol, m.p.  $165$ – $167^\circ$ , see (87).]

*Sulfonation*. [ $\bar{C}$  with fumg.  $\text{H}_2\text{SO}_4$  (65%  $\text{SO}_3$ ) at  $50^\circ$  gives (93% yield (88)) 2,4,6-trichlorophenolsulfonic acid-3.]

*Miscellaneous*. [ $\bar{C}$  with  $\text{SCl}_2 + \text{AlCl}_3$  in  $\text{CS}_2$  or  $\text{CCl}_4$  gives (89) a product, m.p.  $285^\circ$ , which may be 3,3'-dihydroxy-2,4,6,2',4',6'-hexachlorodiphenyl sulfide.]

Reactions of the phenolic group of  $\bar{C}$ . (See also under  $\bar{O}$ 's below.)

*Acidic character of  $\bar{C}$* .  $\bar{C}$  in aq. behaves as an acid and can be titrated with  $N/10$  aq.  $\text{NaOH}$  (3); Neut. Eq. = 197.5. — [Data on dissoc. const. of  $\bar{C}$  include the following: in aq. at  $25^\circ$   $1.0 \times 10^{-7}$  (90),  $3.9 \times 10^{-7}$  (2) cf. (91) (92). — For study of acid strength of  $\bar{C}$  in formamide see (93). — For study of exchange reaction of  $\bar{C}$  with heavy water see (94).]

*Salts of  $\bar{C}$* . [ $\text{NH}_4\bar{A}$ : spar. sol. cold aq., eas. sol. hot aq. (22), somewhat spar. sol. alc. (24); loses  $\text{NH}_3$  in air (12). —  $\text{K}\bar{A}$ ,  $\frac{1}{2}\text{H}_2\text{O}$ : (24) (12). —  $\text{Na}\bar{A}$ : prepn. (95), behavior with  $\text{I}_2$  in various solvents (95) (96), behavior with chloroacetone (3:5425) giving acetonyl 2,4,6-trichlorophenyl ether, m.p.  $75^\circ$  (96).]

$\text{Mg}\bar{A} \cdot 2\text{H}_2\text{O}$ : eas. sol. aq. (12). —  $\text{Ba}\bar{A} \cdot 4\text{H}_2\text{O}$ : spar. sol. aq. (12). —  $\text{Pb}\bar{A}_2$  (12).

$\text{Ag}\bar{A} \cdot \text{H}_2\text{O}$ : yellow (97) [study of decompositions (98) (96) (99)].

*Etherification of  $\bar{C}$* . (See also below under  $\bar{O}$ 's.)

[ $\bar{C}$  with 1,2-dibromoethane (ethylene dibromide) in alk. soln. gives (100)  $\beta$ -bromoethyl 2,4,6-trichlorophenyl ether, m.p. 47–48°. —  $\bar{C}$  with ethylene oxide (1:6105) in alc. NaOEt gives (101)  $\beta$ -hydroxyethyl 2,4,6-trichlorophenyl ether, m.p. 77° (101) (for study of rate of this reaction see (102)) —  $\bar{C}$  (as Na $\bar{A}$ ) with benz-*o*-chlorophenylimino-chloride gives (103) *N*-(*o*-chlorophenyl)benzimidazole 2,4,6-trichlorophenyl ether, m.p. 99–100°, which at 250–270° for 2 hrs. rearr. (103) to the *N*-benzoyl derivative (m.p. 131–132°) of 2,4,6,2'-tetrachloro-diphenylamine. —  $\bar{C}$  with 2,4,6-trichlorobenzyl chloride + NaOH gives (104) 2,4,6-trichlorobenzyl 2,4,6-trichlorophenyl ether, m.p. 101–103°.]

*Esterification of  $\bar{C}$ .* (See also below under  $\bar{C}$ 's.)

[ $\bar{C}$  with  $\text{SOCl}_2$  in pyridine +  $\text{C}_6\text{H}_6$  gives (4) bis-(2,4,6-trichlorophenyl) sulfite, cryst. from  $\text{C}_6\text{H}_6$ , m.p. 87–88°; note, however, that this prod. is unstable and even within a few hours reverts to  $\bar{C}$ .]

[ $\bar{C}$  with  $\text{PCl}_5$  in  $\text{C}_6\text{H}_6$  gives (105) bis-(2,4,6-trichlorophenoxy)phosphoryl chloride,  $(\text{C}_6\text{H}_2\text{OCl}_3)_2\text{P}(\text{O})\text{Cl}$ , cryst. from  $\text{C}_6\text{H}_6$ , m.p. 126–129° (105). (Note that  $\bar{C}$  with  $\text{PCl}_5$  in s.t. at 200–300° gives also (106) some 1,2,3,5-tetrachlorobenzene (3:0915).) —  $\bar{C}$  (3 moles) with  $\text{POCl}_3$  (1 mole) refluxed several days gives (107) tris-(2,4,6-trichlorophenyl) phosphate, m.p. 201° (107).]

[ $\bar{C}$  (2 moles) with  $\text{COCl}_2$  (3:5000) in aq. alk. gives (108) bis-(2,4,6-trichlorophenyl) carbonate, m.p. 153–154° (109).]

① 2,4,6-Trichlorophenyl methyl ether (2,4,6-trichloroanisole) [Beil. VI-192]: cryst. from alc., m.p. 61–62° (9), 60° (110) (111), 59.5° (112); b.p. 240° cor. at 738 mm. (110) cf. (87). [From  $\bar{C}$  with  $\text{Me}_2\text{SO}_4$  + 15% KOH (87); for crystallographic data see (82); for attempted cleavage with pyridine or piperidine see (113); for nitration see (87).]

② 2,4,6-Trichlorophenyl ethyl ether (2,4,6-trichlorophenetole) [Beil. VI-102, VI-104]: m.p. 43–44° (12), b.p. 240° (12). [From  $\text{K}\bar{A}$  +  $\text{EtI}$  (12) or from  $\text{Ag}\bar{A}$  +  $\text{EtI}$  (98).]

— 2,4,6-Trichlorophenyl acetate: oil, b.p. 261–262° (114). [From  $\bar{C}$  with  $\text{AcCl}$  (114).]

③ 2,4,6-Trichlorophenyl benzoate [Beil. IX-117]. m.p. 75.5° (9), 74° (115), 73–74° (6), 70° (14). [From  $\bar{C}$  with benzoyl chloride (3:6240) in pres. of aq. NaOH (115) (9); for study of rate of benzylation of  $\bar{C}$  at 25° and 85° see (116).]

— 2,4,6-Trichlorophenyl *o*-nitrobenzoate: unreported.

— 2,4,6-Trichlorophenyl *m*-nitrobenzoate: unreported.

④ 2,4,6-Trichlorophenyl *p*-nitrobenzoate: m.p. 106° (115).

— 2,4,6-Trichlorophenyl 3,5-dinitrobenzoate: unreported.

⑤ 2,4,6-Trichlorophenyl benzenesulfonate: m.p. 66° (117). [From  $\bar{C}$  with benzenesulfonyl chloride in aq. alk. (117).]

⑥ 2,4,6-Trichlorophenyl *o*-nitrobenzenesulfonate: m.p. 142° (118). [From  $\bar{C}$  with *o*-nitrobenzenesulfonyl chloride +  $\text{K}_2\text{CO}_3$  in acetone (118).]

— 2,4,6-Trichlorophenyl *p*-toluenesulfonate: unreported.

— 2,4,6-Trichlorophenyl phenyl ether: unreported.

⑦ 2,4,6-Trichlorophenyl 2,4-dinitrophenyl ether: m.p. 136° (119). [From  $\bar{C}$  with 2,4-dinitrochlorobenzene in alc. alk. (119).]

— 2,4,6-Trichlorophenyl benzyl ether: unreported.

— 2,4,6-Trichlorophenyl *p*-nitrobenzyl ether: unreported.

⑧ 2,4,6-Trichlorophenyl acetic acid: m.p. 177° (120).

— 2,4,6-Trichlorophenyl *N*-phenylcarbamate: unreported.

⑨ 2,4,6-Trichlorophenyl *N*-(*p*-bromophenyl)carbamate: pl. from  $\text{C}_6\text{H}_6$  +  $\text{EtOAc}$ , m.p. 162–164° cor. (121). [From  $\bar{C}$  with *p*-bromobenzazide (121) in lgr. (121).]

⑩ 2,4,6-Trichlorophenyl *N*-(*p*-iodophenyl)carbamate: m.p. 172–173° (122). [From  $\bar{C}$  with *p*-iodobenzazide (122) in lgr. (122).]



- ① 2,4,6-Trichlorophenyl *N*-(*m*-nitrophenyl)carbamate: white rods from lgr., m.p. 165–167° u.c.; 169–170° cor. (123). [From  $\bar{C}$  with *m*-nitrobenzazide (123) in lgr. (123).]
- ② 2,4,6-Trichlorophenyl *N*-(*p*-nitrophenyl)carbamate: pale yel. rods from lgr., m.p. 166° cor. (124). [From  $\bar{C}$  with *p*-nitrobenzazide (124) in lgr. (124).]
- 2,4,6-Trichlorophenyl *N*-(3,5-dinitrophenyl)carbamate: unreported.
- ③ 2,4,6-Trichlorophenyl *N*-(3,5-dinitro-4-methylphenyl)carbamate: yel. pr. from lgr. or EtOAc, m.p. 195–196° u.c., 201–202° cor. (125). [From  $\bar{C}$  with 3,5-dinitro-4-methylbenzazide (125) in lgr. (125).]
- 2,4,6-Trichlorophenyl *N*-( $\alpha$ -naphthyl)carbamate: unreported.
- ④ 2,4,6-Trichlorophenyl *N*-( $\beta$ -naphthyl)carbamate: pr. from lgr., m.p. 157–158° u.c., 161–162° cor. (126). [From  $\bar{C}$  with  $\beta$ -naphthyl isocyanate (126) or  $\beta$ -naphthazide (126) in lgr. (126).]
- ⑤ 2,4,6-Trichlorophenyl *N,N*-diphenylcarbamate: m.p. 143° (127). [From  $\bar{C}$  with *N,N*-diphenylcarbamyl chloride (127).]

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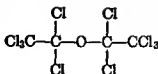
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3:1676 DECACHLORODIETHYL  
ETHER  
(bis-(Pentachloroethyl) ether;  
"Perchloroether")



$\text{C}_4\text{OCl}_{10}$  Beil. II-210  
II<sub>1</sub>—  
II<sub>2</sub>—

M.P. 69° (1)

$D_{25}^{145} = 1.900$  (2)

[For crystallog. data see (3).]

[For prepn. of  $\bar{\text{C}}$  from nbs. diethyl ether (1:6116) with excess dry  $\text{Cl}_2$  in direct sunlight see (1).]

$\bar{\text{C}}$  on boilg. decomposes (2) into trichloroacetyl chloride (3:5420) and hexachloroethane (3:4835).

$\bar{\text{C}}$  with conc.  $\text{H}_2\text{SO}_4$  at 240° is slowly attacked yielding (2) trichloroacetyl chloride (3:5420).

$\bar{\text{C}}$  with alc.  $\text{K}_2\text{S}$  loses 2 atoms of chlorine yielding (2) di-(trichlorovinyl) ether (3:6373).

$\bar{\text{C}}$  with metallic potassium on htg. detonates; in this behavior  $\bar{\text{C}}$  behaves toward alkali metals like many other highly halogenated compounds.

Note that all these data on  $\bar{\text{C}}$  are very old; no later studies of  $\bar{\text{C}}$  are reported in the literature.

3:1676 (1) Regnault, *Ann.* 34, 27-29 (1840). (2) Malaguti, *Ann. chim.* (3) 16, 13-28 (1846). (3) Nickles, *Ann. chim.* (3) 22, 29 (1848).

3:1685 CHLOROPROPIONIC ACID  $\text{Cl.C}\equiv\text{C.COOH}$   $\text{C}_2\text{HO}_2\text{Cl}$  Beil. II-478  
II<sub>1</sub>—  
II<sub>2</sub>-(451)

M.P. 69-70° (1)

Colorless cryst. from pet. eth.; eas. sol. ether; eas. vol. (even in desiccator). Very irritating and poisonous; salts extremely toxic (1). — Stable in dry state at room temperature.

[For prepn. from propionic ac. [Beil. II-477] by actn. of  $\text{KOH/KOCl}$  soln. at 0° see (1) (2).]

$\bar{\text{C}}$  on htg. with  $\text{Ba}(\text{OH})_2$  soln. yields chloroacetylene (3:7000) +  $\text{BaCO}_3$  while acidification and ether extraction of the aq. layer yields malonic ac. (1:0480), m.p. 133-134° (1). [An alk. soln. of  $\bar{\text{C}}$  on stdg. is also partly converted to malonic ac. (1).]

3:1685 (1) Straus, Kollek, Heyn, *Ber.* 63, 1876-1877 (1930). (2) Brit. 333,946, Sept. 18, 1930; *Cent.* 1931, I 523.

3:1687 2,3,4,6-TETRACHLOROPHENOL



$\text{C}_6\text{H}_2\text{OCl}_4$  Beil. VI-193  
VI<sub>1</sub>—  
VI<sub>2</sub>-(182)

M.P. 70° (1) (2) (3)

60-70° (4)

68-69° (5) (6)

67.5-68° (7)

67-60° (8)

67-68° (9)

67° (10) (11)

65.5° (12)

65-66° (13)

B.P. 164° at 23 mm. (4)

160.5° at 21 mm. (4)

159° at 20 mm. (4)

157° at 19 mm. (4)

155° at 18 mm. (4)

152.5° at 17 mm. (4)

150° at 16 mm. (4)

Ndls. from lgr., AcOH, or ether. — Almost insol. cold aq.; spar. sol. hot aq.; but volatile with steam. — Eas. sol. alc.,  $C_6H_6$ ,  $CHCl_3$ ,  $CS_2$ , lgr.; fairly sol. hot pet. eth. — Odorless at ord. temp.

### PREPARATION OF $\bar{C}$

[For prepn. of  $\bar{C}$  from phenol (1:1420) with  $Cl_2$  at  $80^\circ$  for 14 days (7) or with  $Cl_2$  in pres. of 2-3%  $I_2$  or 4-5%  $SbCl_3$  or 5-6%  $FeCl_3$  for shorter periods (7), from sodium phenolate with  $SO_2Cl_2$  (13), or from 2,4,6-trichlorophenol (3:1673) with  $Cl_2$  (1) in pres. of  $I_2$  at  $40^\circ$  (8) or with  $Cl_2$  in  $CCl_4$  soln. in pres. of  $FeCl_3$  (14), see indic. refs.]

[For formn. of  $\bar{C}$  from 3,5,6-trichloro-2-hydroxybenzoic acid (3,5,6-trichlorosalicylic acid) (5) with  $Cl_2$  in 30% AcOH see (5); from 2,4,5,6-tetrachloro-3-hydroxybenzoic acid [Beil. X-144] (11) by htg. with lime see (11); from 2,4,5,6-tetrachloro-3-hydroxybenzaldehyde (6) with 50% aq. KOH at  $100^\circ$  for 2 hrs. (the CO group being eliminated as K formate) see (6); from  $\alpha$ -(2,4,5,6-tetrachloro-3-hydroxybenzoyl)benzoic acid (3) by cleavage with conc.  $H_2SO_4$  see (3)]

[For formn. of  $\bar{C}$  from 1,2,4,4,5,6,6-heptachlorocyclohexen-1-one-3 [Beil. VII-51] by reduction with  $SnCl_2/HCl/AcOH$  (4) or with  $KI/AcOH$  or  $Na_2SO_3/AcOH$  see (12); from "6-hydroxyphenylene diazosulfide" with  $Cl_2$  in AcOH followed by reduction with  $SnCl_2$  see (10).]

### USES OF $\bar{C}$ (OR ITS SALTS)

[For patents on use of  $\bar{C}$  (or its salts) as bactericide (15) (16) in preservation of rubber latex (17), as insecticide (18), or in triphenyl phosphate as wood preservative (19) see indic. refs.]

[For general articles on  $\bar{C}$  (or its salts) as bactericides (20), fungicides (21) (27) for paint (22) or leather (23) (24) (25) (26), or in preservation of brine samples for analysis (28) see indic. refs.]

### PHYSIOLOGICAL EFFECTS OF $\bar{C}$ (OR ITS SALTS)

[For studies on dermatitis from  $\bar{C}$  or its salts see (29) (30); for report on toxicity of  $\bar{C}$  in leather see (31).]

### CHEMICAL BEHAVIOR OF $\bar{C}$

Action of chlorine. [ $\bar{C}$  with  $Cl_2$  in AcOH gives (4) (12) 1,2,4,4,5,6,6-heptachlorocyclohexen-1-one-3 [Beil. VII-51].]

Action of bromine.  $\bar{C}$  with  $Br_2$  (1 mole) in pres. of Fe powder gives (8) 5-bromo-2,3,4,6-tetrachlorophenol [Beil. VI-1(106)], cryst. from AcOH, m.p.  $197^\circ$  (8) (32),  $192^\circ$  (33) (corresp. acetyl deriv., m.p.  $144^\circ$  (33); corresp. benzoyl deriv., m.p.  $169^\circ$  (33)).

Action of nitric acid. [ $\bar{C}$  with fuming  $HNO_3$  (5 wt. parts) is oxidized (70% yield (4)) (12) to 2,3,5-trichlorobenzoquinone-1,4 (3:4672). — Note, however, that the mononitro deriv. of  $\bar{C}$ , viz., 5-nitro-2,3,4,6-tetrachlorophenol, ndls. from  $C_6H_6$ , m.p.  $122^\circ$ , has been ohtd. (8) by HBr cleavage of the corresp. methyl ether (see below).]

Behavior of  $\bar{C}$  as an acid.  $\bar{C}$  in aq. behaves as an acid,  $K$  at  $25^\circ = 4.2 \times 10^{-6}$  (2) cf. (34), and can be titrated with  $N/10$  aq. NaOH (1); Neut. Eq. = 232. — [For prepn. of alk. salts of  $\bar{C}$  by neutralization in mixtures of org. solvents see (35); for uses of salts of  $\bar{C}$  see above.]

Miscellaneous reactions of  $\bar{C}$ . [ $\bar{C}$  (as  $K\bar{A}$ ) in conc. aq. soln with  $COCl_2$  (3:5000) in toluene gives (36) bis-(2,3,4,6-tetrachlorophenyl) carbonate, m.p.  $155-156^\circ$  (36).]

- ① 2,3,4,6-Tetrachlorophenyl methyl ether (2,3,4,6-tetrachloroanisole): ndls. from MeOH, m.p. 64-65° (4), 60° (8), b.p. 266-270° u.c. at 244 mm. (8). [From  $\bar{C}$  with MeI in MeOH/NaOMe soln. (4) cf. (8). — Note that this prod. on nitration with 7-8 wt. pts. fuming  $HNO_3$  gives 5-nitro-2,3,4,6-tetrachloroanisole, m.p. 58° (8).]
- ② 2,3,4,6-Tetrachlorophenyl ethyl ether (2,3,4,6-tetrachlorophenetole): ndls. from alc., m.p. 59-60° (4), 55° (6). [From  $\bar{C}$  with EtI in EtOH/NaOEt soln. (4); also indirectly (6).]
- ③ 2,3,4,6-Tetrachlorophenyl acetate: cryst. from alc., m.p. 66° (5), 65-66° (4), 59° (12). [From  $\bar{C}$  with  $Ac_2O$  (4) or with AcCl (12).]
- ④ 2,3,4,6-Tetrachlorophenyl benzoate: cryst. from alc., m.p. 116° (10) (13) (3), 115° (4), 114.5° (12), 113-115° (11). [From  $\bar{C}$  as NaA with BzCl (4). — Note that this prod. depresses m.p. (110°) of the corresp. benzoate from 2,3,4,5-tetrachlorophenol (3:3523) (9).]
- ⑤ 2,3,4,6-Tetrachlorophenyl *N*-phenylcarbamate: ndls. from alc., m.p. 141-142° (4). [From  $\bar{C}$  with phenyl isocyanate in  $C_6H_6$  24 hrs. at room temp. (4).]

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## 3:1090 2,6-DICHLOROBENZALDEHYDE

 $C_7H_4OCl_2$ Beil. VII - 237  
VII<sub>1</sub>-(134)

M.P. 71° (1)  
70-71° (2)  
70° (3)  
69-70° (4) (5)

Colorless cryst. from pet. ether (b.p. 40–60°) or lgr.

[For prepn. of  $\bar{C}$  from 2,6-dichlorotoluene (3:6270) by oxidn. with  $MnO_2 + H_2SO_4$  see (2); for prepn. of  $\bar{C}$  from 2,6-dichlorobenzaldehyde diethylacetal (see below) by hydrolysis on shaking with dil. HCl see (6)]

[ $\bar{C}$  on reduction would presumably yield 2,6-dichlorobenzyl alc., but this prod. is unreported in the literature.]

$\bar{C}$  in alk. suspension on oxidn. with air gives (7) 2,6-dichlorobenzoic acid (3:4200), m.p. 144°.

[ $\bar{C}$  (fused) with  $Cl_2$  in brilliant artificial light gives (58% yield (8)) 2,6-dichlorobenzoyl chloride, b.p. 126–128° at 18 mm. —  $\bar{C}$  with  $PCl_5$  at 160° gives (90% yield (9)) (4) (5) 2,6-dichlorobenzal (di)chloride (3:9398) oil, b.p. 124–126° at 16 mm. (9), accompanied in some preparations (4) (5) by some bis-( $\alpha$ ,2,6-trichlorobenzyl) ether, m.p. 180–185° (4) (5).]

[ $\bar{C}$  with alkali sulfite (1 mole) under press. reacts at one of the two halogen atoms giving (2) 6-chlorobenzaldehydesulfonic acid-2 [Beil. XI-324] —  $\bar{C}$  with alkali sulfite (2 moles) under press. gives (2) benzaldehyde disulfonic acid-2,6 [Beil. XI-326]]

$\bar{C}$  dissolvd. in 7–8 wt. pts. conc.  $H_2SO_4$ , and at 10–15° mononitrated with a mixt. of fuming  $HNO_3 +$  conc.  $H_2SO_4$  poured into aq. gives (yield not stated (10)) (2) 2,6-dichloro-3-nitrobenzaldehyde [Beil. VII-263], pl. from  $CS_2$  (10) or lfts. from  $C_6H_6$  (2), m.p. 76° (10), 76–77° (2) (corresp.  $\alpha$ -oxime, m.p. 156–157° (10),  $\beta$ -oxime, m.p. 154–155° (10); note that a mixt. of the two oximes melts 128–130° (10)) — [Note that no dinitro-2,6-dichlorobenzaldehyde has been reported; also that the m.p.'s of certain of the isomeric mononitrodichlorobenzaldehydes are very close to the above mononitration prod.: e.g., 2,4-dichloro-6-nitrobenzaldehyde (from 2,4-dichlorobenzaldehyde 3:1800) has m.p. 74–75°; 2,5-dichloro-3-nitrobenzaldehyde (from 2,5-dichlorobenzaldehyde 3:1145) has m.p. 66.5–67°; 3,4-dichloro-6-nitrobenzaldehyde (from 3,4-dichlorobenzaldehyde 3:0350) has m.p. 73°.]

[ $\bar{C}$  on sulfonation gives (2) 2,6-dichlorobenzaldehydesulfonic acid-3 [Beil. XI-325].]

[ $\bar{C}$  with 50% KOH at 100° for 5 hrs. under  $N_2$  undergoes cleavage of the aldehyde group giving (84% yield (11)) *m*-dichlorobenzene (3.5960) q.v. and the corresp. K formate.]

[ $\bar{C}$  with aq. alc. hydrazine sulfate gives (86% yield (18)) 2,6-dichlorobenzaldazine, m.p. 153° cor.; but this prod. or  $\bar{C}$  with hydrazine hydrate refluxed 5 hrs. gives 2,6-dichlorobenzaldehyde hydrazone, m.p. 134°, which by Wolff-Kishner reduction gives (80% yield (18)) 2,6-dichlorotoluene (3:6270).]

[ $\bar{C}$  with EtOH contg. 1½ wt. % dry HCl refluxed 24 hrs. gives (13.6% yield (6)) 2,6-dichlorobenzaldehyde diethylacetal, oil, b.p. 142–144° at 10 mm., m.p. –1° (6); this prod. with dil. HCl readily hydrolyzes back to  $\bar{C} +$  EtOH.]

[ $\bar{C}$  with  $\beta$ -naphthol (2 moles) in AcOH with 30% HBr in AcOH at 100° for 2 hrs. or at room temp. for 24 hrs. condenses and ring-closes giving (88% yield (8)) 9-(2,6-dichlorophenyl)-1,2,7,8-dibenzoxanthene ( $C_{27}H_{16}OCl_2$ ), cryst. from lgr., m.p. 264–265° (8). — Note that  $\bar{C}$  with  $\beta$ -thionaphthol (2 moles) under similar conditions yields a prod.  $C_{27}H_{16}S_2Cl_2$ , of unknown structure.]

$\bar{C}$  with anhydrous NaOAc +  $Ac_2O$  in Perkin synthesis (12) (13) (1), or  $\bar{C}$  with malonic acid in AcOH (13) gives (yields: 81–83% (12), 80% (1), 18% (13)) 2,6-dichlorocinnamic acid [Beil. IX-1-(239)], cryst. from AcOH, m.p. 196° (12), 193° (13), 183° (1); note that in this reaction some 2,6-dichlorobenzal diacetate [Beil. VII-1-(134)], ndla. from lgr., m.p. 85° (1), is sometimes formed.

$\bar{C}$  appears to behave normally with  $RMgX$  reactants [e.g.,  $\bar{C}$  with  $MeMgI$  in dry ether followed by usual hydrolysis gives (68.6% yield (14)) 2,6-dichlorophenyl-methyl-carbinol,

m.p. 34-35°, h.p. 137-138° at 17 mm., 134-136° at 13 mm. (corresp. benzoate, m.p. 77°);  $\bar{C}$  with  $C_6H_5MgBr$  similarly gives in good yield (1) 2,6-dichlorophenyl-phenyl-carbinol, m.p. 57° (corresp. acetate, m.p. 105°). [For conversion of  $\bar{C}$  to 2,6-dichlorostyrene (16) (17) via formn. of 2,6-dichlorophenyl-methyl-carbinol (above) and dehydration of latter with  $KHSO_4$  (31.5% yield (16)) see indic. refs.]

$\bar{C}$  with aniline readily condenses yielding (1) 2,6-dichlorobenzaldehyde anil, m.p. 64-65°.

② 2,6-Dichlorobenzaldoxime: colorless ndls. from  $C_6H_6$  (10) or lgr. (1), m.p. 149-150° (10), 146-147° (1). [From  $\bar{C}$  with  $NH_2OH.HCl + Na_2CO_3$  in dil. alc. at 100° for 5 hrs. (10) cf. (1); with cold  $Ac_2O$  this prod. gives an acetyl deriv., m.p. 51° (10); with boilg.  $Ac_2O$  for 5 min. the oxime loses  $H_2O$  giving (1) 2,6-dichlorobenzonitrile [Beil. IX-343, IX<sub>1</sub>-(141)], ndls. from lgr. or by sublimation, m.p. 143° (1), 144.5-146.5° (15).]

— 2,6-Dichlorobenzaldehyde phenylhydrazone: unreported.

— 2,6-Dichlorobenzaldehyde o-nitrophenylhydrazone: m.p. 154° (1).

— 2,6-Dichlorobenzaldehyde p-nitrophenylhydrazone: unreported.

— 2,6-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

— 2,6-Dichlorobenzaldehyde p-bromophenylhydrazone: m.p. 142° (1).

— 2,6-Dichlorobenzaldehyde semicarbazone: unreported.

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### 3:1700 1-CHLORONAPHTHOL-2



$C_{10}H_7OCl$

Beil. VI - 648

VI<sub>1</sub>—

VI<sub>2</sub>-(603)

M.P. 72° (1)

71° (2)

70-71° (3)

70° (4) (11) (20) (27)

68-69° (5)

68° (8)

Ndls. from hot aq., ndls. from lgr., pr. from  $CHCl_3$ ; eas. sol. alc.,  $AcOH$ ,  $C_6H_6$ ,  $CHCl_3$ , hoilg. lgr. — For crystallographic constants see (4). — Volatile with steam.

[For prepn. of  $\bar{C}$  from  $\beta$ -naphthol (1:1540) with  $Cl_2$  in  $AcOH$  (80% yield (21)) (3) (4) (6), with  $SO_2Cl_2$  in  $CS_2$  (7) or with  $C_6H_5ICl_2$  (84% yield (2)) see indic. refs.; from sodium  $\beta$ -naphtholate in  $CS_2$  suspension on treatment with  $Cl_2$  (8) or in cold aq. with  $NaOCl$  (84% yield (5)) (9) see indic. refs.; for formn. of  $\bar{C}$  from  $\beta$ -naphthol (1:1540) as hy-prod. of its

oxidn. with  $\text{FeCl}_3$  to  $\beta$ -dinaphthol (2,2'-dihydroxybinaphthyl-1,1') see (10) (11) (the proportion of  $\bar{C}$  increases with increasing acidity (11)); for formn. of  $\bar{C}$  from  $\beta$ -naphthol as by-prod. of react. with  $\text{SeOCl}_2$  see (20) ]

$\bar{C}$  with 1 mole  $\text{Cl}_2$  in  $\text{AcOH}$  soln. gives (12) 1,6-dichloronaphthol-2 (3:3600), m.p. 119.5° (12);  $\bar{C}$  with 1 mole  $\text{Br}_2$  yields (7) (13) 6-bromo-2-chloronaphthol-2 [Beil. VI-651], ndls. from  $\text{AcOH}$  with 1 mole solvent, r.o.p. 92°, anhydrous ndls. by sublimation, m.p. 101° (7). [Note, however, that  $\bar{C}$  in  $\text{AcOH} + \text{NaOAc}$  with 1 mole  $\text{Br}_2$  yields (1) "1-bromo-1-chloro-2-oxonaphthalenedihydride-1,2," pale yel. pr. from lgr., m.p. 90° when pure but on short stdg. soon becoming lower ]

[ $\bar{C}$  in  $\text{AcOH}$  with conc.  $\text{HI}$  ( $D = 1.5$ ) boiled 5 hrs gives (79% yield (5))  $\beta$ -naphthol (1:1540), m.p. 121° (5); note, however, that  $\bar{C}$  is unaffected by  $\text{SnCl}_2$  either in acid or alk. even after protracted refluxing, but in  $\text{AcOH}/\text{HCl}$  in s.t. 8 hrs. at 100° (1) reduces to  $\beta$ -naphthol ]

[ $\bar{C}$  in alk. soln. treated with  $p$ -nitrobenzenediazonium chloride soln loses its halogen atom and yields (14) (15) (16) cf. (21) 1-( $p$ -nitrobenzeneazo)naphthol-2 ("Para Red") [Beil. XVI-165, XVI-1-(255)], red ndls from pyridine, m.p. 246-247° u.c. (14), from  $\text{AcOH}$ , m.p. 250° cor. (15). (Note, however, that as much as 40% of a light yel. by-prod., m.p. 125° dec., is also formed (16) )]

[ $\bar{C}$  melted with  $\text{PCl}_5$  and then treated with aq. (4), or  $\bar{C}$  in alk. soln shaken with  $\text{POCl}_3$  (17), or sodium salt of  $\bar{C}$  shaken in xylene with  $\text{POCl}_3$  (18), yields *tris*-(1-chloronaphthyl-2) phosphate, ndls from alc., m.p. 152° (4) (note that by the second method (above) *bis*-(1-chloronaphthyl-2)phosphoric acid, ndls. from alc. +  $\text{HCl}$ , m.p. 251° (4), is also formed (4))]

[ $\bar{C}$  (2 moles) with  $\text{Na}_2\text{S}$  (1 mole) htd. in aq. under  $\text{N}_2$  gives (97.5% yield (10)) *bis*-(2-hydroxynaphthyl-1) sulfide [Beil. VI-976, VI-1-(470)], colorless cryst. from  $\text{AcOH}$ , m.p. 226° cor. (10).]

$\bar{C}$  under many circumstances yields ethers with difficulty and small yields; e.g.,  $\bar{C}$  with  $\text{MeOH} + \text{conc. H}_2\text{SO}_4$  (25) or  $p$ -toluenesulfonic acid (26) gives only 2-7% methyl ether; however,  $\bar{C}$  in  $\text{MeOH}/\text{KOH}$  htd. with  $\text{MeI}$  in s.t. at 100° for 5 hrs. (25), or  $\bar{C}$  in 15%  $\text{KOH}$  shaken with  $\text{Me}_2\text{SO}_4$  for  $\frac{1}{2}$  hr. (91% yield (5)), gives 1-chloro-2-methoxynaphthalene, pr. from alc., m.p. 70-71° (5), 68° (25), 78° (27); this methyl ether on protracted htg. with conc.  $\text{HCl}$  in s.t. at 200-250° yields  $\bar{C} + \text{MeCl}$  (17) (27). —  $\bar{C}$  with  $\text{EtOH} + \text{conc. H}_2\text{SO}_4$  (25) gives only 0.5-10% ethyl ether, but  $\bar{C}$  with  $\text{EtOH}/\text{KOH} + \text{EtBr}$  htd. 3 hrs. at 100° (25) gives 1-chloro-2-ethoxynaphthalene, lts. from alc., m.p. 58° (25).

③ 1-Chloro-2-naphthyl acetate: tbs. from alc., m.p. 42-43° (3). [From  $\bar{C}$  with  $\text{AcCl}$  (3).]

④ 1-Chloro-2-naphthyl benzoate: lts. from alc., m.p. 101° (27). [From  $\bar{C}$  in alk. soln by shaking with  $\text{BzCl}$  (27)]

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m.p. 34-35°, h.p. 137-138° at 17 mm., 134-136° at 13 mm. (corresp. benzoate, m.p. 77°);  $\bar{C}$  with  $C_6H_5MgBr$  similarly gives in good yield (1) 2,6-dichlorophenyl-phenyl-carbinol, m.p. 57° (corresp. acetate, m.p. 105°). [For conversion of  $\bar{C}$  to 2,6-dichlorostyrene (16) (17) via formn. of 2,6-dichlorophenyl-methyl-carbinol (above) and dehydration of latter with  $KHSO_4$  (31.5% yield (16)) see indic. refs.]

$\bar{C}$  with aniline readily condenses yielding (1) 2,6-dichlorohenzaldehyde anil, m.p. 64-65°.

Ⓐ 2,6-Dichlorohenzaldoxime: colorless ndls. from  $C_6H_6$  (10) or lgr. (1), m.p. 149-150° (10), 146-147° (1). [From  $\bar{C}$  with  $NH_2OH.HCl + Na_2CO_3$  in dil. alc. at 100° for 5 hrs. (10) cf. (1); with cold  $Ac_2O$  this prod. gives an acetyl deriv., m.p. 51° (10); with boilg.  $Ac_2O$  for 5 min. the oxime loses  $H_2O$  giving (1) 2,6-dichlorobenzonitrile [Beil. IX-343, IX-1(141)], ndls. from lgr. or by sublimation, m.p. 143° (1), 144.5-146.5° (15).]

— 2,6-Dichlorohenzaldehyde phenylhydrazone: unreported.

— 2,6-Dichlorohenzaldehyde o-nitrophenylhydrazone: m.p. 154° (1).

— 2,6-Dichlorohenzaldehyde p-nitrophenylhydrazone: unreported.

— 2,6-Dichlorohenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

— 2,6-Dichlorohenzaldehyde p-bromophenylhydrazone: m.p. 142° (1).

— 2,6-Dichlorohenzaldehyde semicarbazone: unreported.

3:1690 (1) Reich, Salzmann, Kawa, *Bull. soc. chim.* (4) 21, 217-225 (1917). (2) Geigy and Co., Ger. 199,943, July 4, 1908; *Cent.* 1908, II 363-364; [C.A. 2, 3909 (1908)]. (3) Lock, *Ber.* 66, 1530 (1933). (4) Olivier, Weber, *Rec. trav. chim.* 52, 169-174 (1933). (5) Olivier, Weber, *Rec. trav. chim.* 53, 882 (1934). Sept. 4, 1936; *Cent.* 1936, II 36. *Chem.* (2) 152, 68-72 (1930). Theilacker, Beisswenger, *Ann.* 495, 254 (1932).

(11) Lock, *Ber.* 66, 1530 (1933). (12) Bock, Lock, Schmidt, *Monatsh.* 64, 401-402, 407-408 (1934). (13) Willstädt, *Ber.* 64, 2692 (1931). (14) Lock, Böck, *Ber.* 70, 921 (1937). (15) Norris, Klemka, *J. Am. Chem. Soc.* 62, 1433 (1940). (16) Marvel, Overberger, Allen, Johnston, Saunders, Young, *J. Am. Chem. Soc.* 68, 863 (1946). (17) Michalek, Clark, *Chem. & Eng. News* 22, 1559-1563 (1945). (18) Lock, Stach, *Ber.* 76, 1252-1256 (1943).

### 3:1700 1-CHLORONAPHTHOL-2


 $C_{10}H_7OCl$ 

Beil. VI - 648

 $VI_1-$ 
 $VI_2-(603)$ 

M.P. 72° (1)

71° (2)

70-71° (3)

70° (4) (11) (20) (27)

68-69° (5)

68° (8)

Ndls. from hot aq., ndls. from lgr., pr. from  $CHCl_3$ ; eas. sol. alc.,  $AcOH$ ,  $C_6H_6$ ,  $CHCl_3$ , boilg. lgr. — For crystallographic constants see (4). — Volatile with steam.

[For prepn. of  $\bar{C}$  from  $\beta$ -naphthol (1:1540) with  $Cl_2$  with  $SO_2Cl_2$  in  $CS_2$  (7) or with  $C_6H_5ICl_2$  (84% yield naphtholate in  $CS_2$  suspension on treatment with  $Cl_2$  yield (5)) (9) see indic. refs.; for formn. of  $\bar{C}$  from  $\beta$ -naphthol (1:1540) as by-prod. of its

oxdn. with  $\text{FeCl}_3$  to  $\beta$ -dinaphthol (2,2'-dihydroxybinaphthyl-1,1') see (10) (11) (the proportion of  $\bar{C}$  increases with increasing acidity (11)); for formn. of  $\bar{C}$  from  $\beta$ -naphthol as by-prod. of react. with  $\text{SeOCl}_2$  see (20).]

$\bar{C}$  with 1 mole  $\text{Cl}_2$  in  $\text{AcOH}$  soln. gives (12) 1,6-dichloronaphthol-2 (3:3600), m.p. 119.5° (12);  $\bar{C}$  with 1 mole  $\text{Br}_2$  yields (7) (13) 6-bromo-2-chloronaphthol-2 [Beil. VI-651], ndls. from  $\text{AcOH}$  with 1 mole solvent, m.p. 92°, anhydrous ndls. by sublimation, m.p. 101° (7). [Note, however, that  $\bar{C}$  in  $\text{AcOH} + \text{NaOAc}$  with 1 mole  $\text{Br}_2$  yields (1) "1-bromo-1-chloro-2-oxonaphthalenedihydride-1,2," pale yel. pr. from lgr., m.p. 90° when pure but on short stdg. soon becoming lower]

[ $\bar{C}$  in  $\text{AcOH}$  with conc.  $\text{HI}$  ( $D = 1.5$ ) boiled 5 hrs. gives (79% yield (5))  $\beta$ -naphthol (1:1540), m.p. 121° (5); note, however, that  $\bar{C}$  is unaffected by  $\text{SnCl}_2$  either in acid or alk. even after protracted refluxing, but in  $\text{AcOH}/\text{HCl}$  in s.t. 8 hrs. at 100° (1) reduces to  $\beta$ -naphthol.]

[ $\bar{C}$  in alk. soln. treated with *p*-nitrobenzenediazonium chloride soln. loses its halogen atom and yields (14) (15) (16) cf. (21) 1-(*p*-nitrobenzeneazo)naphthol-2 ("Para Red") [Beil. XVI-165, XVI-1-(255)], red ndls. from pyridine, m.p. 246-247° u.c. (14), from  $\text{AcOH}$ , m.p. 250° cor. (15) (Note, however, that as much as 40% of a light yel. by-prod., m.p. 125° dec., is also formed (16).)]

[ $\bar{C}$  melted with  $\text{PCl}_3$  and then treated with aq. (4), or  $\bar{C}$  in alk. soln. shaken with  $\text{POCl}_3$  (17), or sodium salt of  $\bar{C}$  shaken in xylene with  $\text{POCl}_3$  (18), yields *tris*-(1-chloronaphthyl-2) phosphate, ndls. from alc., m.p. 152° (4) (note that by the second method (above) *bis*-(1-chloronaphthyl-2)phosphoric acid, ndls. from alc. +  $\text{HCl}$ , m.p. 251° (4), is also formed (4)).]

[ $\bar{C}$  (2 moles) with  $\text{Na}_2\text{S}$  (1 mole) htd. in aq. under  $\text{N}_2$  gives (97.5% yield (19)) *bis*-(2-hydroxynaphthyl-1) sulfide [Beil. VI-976, VI-1-(470)], colorless cryst. from  $\text{AcOH}$ , m.p. 226° cor. (19).]

[ $\bar{C}$  on refluxing a few hrs. with aniline (best under  $\text{N}_2$  (23)) yields (22) 1-anilinonaphthol-2 [Beil. XIII-678], ndls. from lgr., m.p. 153-154° (22), 155-156° (23); for corresp. reactn. with many other monamines (22) (23) and diamines (24) see indic. refs.]

$\bar{C}$  under many circumstances yields ethers with difficulty and small yields; e.g.,  $\bar{C}$  with  $\text{MeOH} + \text{conc. H}_2\text{SO}_4$  (25) or *p*-toluenesulfonic acid (26) gives only 2-7% methyl ether; however,  $\bar{C}$  in  $\text{MeOH}/\text{KOH}$  htd. with  $\text{MeI}$  in s.t. at 100° for 5 hrs. (25), or  $\bar{C}$  in 15%  $\text{KOH}$  shaken with  $\text{Me}_2\text{SO}_4$  for  $\frac{1}{2}$  hr. (91% yield (5)), gives 1-chloro-2-methoxynaphthalene, pr. from alc., m.p. 70-71° (5), 68° (25), 78° (27); this methyl ether on protracted htg. with conc.  $\text{HCl}$  in s.t. at 200-250° yields  $\bar{C} + \text{MeCl}$  (17) (27). —  $\bar{C}$  with  $\text{EtOH} + \text{conc. H}_2\text{SO}_4$  (25) gives only 0.5-10% ethyl ether, but  $\bar{C}$  with  $\text{EtOH}/\text{KOH} + \text{EtBr}$  htd. 3 hrs. at 100° (25) gives 1-chloro-2-ethoxynaphthalene, lfts. from alc., m.p. 58° (25).

③ 1-Chloro-2-naphthyl acetate: this, from alc., m.p. 42-43° (3). [From  $\bar{C}$  with  $\text{AcCl}$  (3).]

④ 1-Chloro-2-naphthyl benzoate: lfts. from alc., m.p. 101° (27). [From  $\bar{C}$  in alk. soln. by shaking with  $\text{BzCl}$  (27).]

3:1700 (1) Fries, Schummelschmidt, *Ann.* 484, 293, 296-297 (1930). (2) Neu, *Ber.* 72, 1511 (1939). (3) Zincke, *Ber.* 21, 3384-3385 (1888). (4) Cleve, *Ber.* 21, 895-896 (1888). (5) Franzen, Stäuble, *J. prakt. Chem.* (2) 103, 379-380 (1921/22). (6) Clifford (to Goodyear Tire and Rubber Co.), *Brit.* 302,147, Feb. 6, 1929, *Cent.* 1929, 1 1867. (7) Armstrong, Rossiter, *Chem. News* 59, 225 (1859). *Ber.* 24, Referate, 705 (1891). (8) Schall, *Ber.* 16, 1901 (1883). (9) Kalle and Co., *Ger.* 165,821, March 16, 1906, *Cent.* 1906, 1 1307. (10) Ioffe, *J. Gen. Chem. (U.S.S.R.)* 7, 2715-2718 (1937), *Cent.* 1939, II 4475; *C.A.* 32, 2931 (1938). (11) Ioffe, Kuznetsov, Litovskii, *J. Gen. Chem. (U.S.S.R.)* 5, 1655-1656 (1935); *Cent.* 1937,

fabrikation, Ger. 246,871, May 11, 1912; *Cent.* 1912, I 1875. (19) Ringeissen, *Compt. rend.* 198, 2182 (1934); *Cent.* 1934, II 2677; *C.A.* 28, 5432. (20) Morgan, Burstall, *J. Chem. Soc.* 1928, 3269.

(21) Pollak, Gebauer-Fulnegg, *Monatsh.* 59, 317 (1928). (22) Wahl, Lantz, Ger. 365,367, 368, 1922; *Beil.* 1922, 546, 440. Jan. 15, 1922; *Cent.* 1922, II 697, 698.

34-37 (1895).

3:1745 4,6-DICHLORO-3-METHYLPHENOL  $\text{OH}$   $\text{C}_7\text{H}_5\text{OCl}_2$  *Beil.* S.N. 526  
(4,6-Dichloro-*m*-cresol)



M.P. 71.5-72° (1) B.P. 235-236° (1)

$\bar{\text{C}}$  is volatile with steam. — The products of m.p. 45-46° (2) and m.p. 58° (3) formerly supposed to have been  $\bar{\text{C}}$  are now regarded (1) as 2,4,6-trichloro-3-methylphenol (3:0618) and 2,4-dichloro-3-methylphenol (3:1205) respectively.

[For prepn. of  $\bar{\text{C}}$  from 6-amino-4-chloro-3-methylphenol (1) via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reaction see (1); from 4,6-diamino-3-methylphenol (1) via tetrazotization and use of  $\text{Cu}_2\text{Cl}_2$  reaction see (1); for formn. of  $\bar{\text{C}}$  (together with other isomers) from 4-chloro-3-methylphenol (3:1535) or from 6-chloro-3-methylphenol (3:0700) in  $\text{CHCl}_3$  with  $\text{Cl}_2$  (1 mole) see (1).]

$\bar{\text{C}}$  in  $\text{CHCl}_3$  with 1 mole  $\text{Cl}_2$  gives alm. quant. yields (1) 2,4,6-trichloro-3-methylphenol (3:0618), m.p. 46° (1).

① 4,6-Dichloro-3-methylphenyl benzoate: mats of very fine ndls. from alc., m.p. 57.5° (1). [From  $\bar{\text{C}}$  with  $\text{BzCl}$  in pyridine (1).]

② 4,6-Dichloro-3-methylphenyl benzenesulfonate: thin lustrous plates from alc., m.p. 86° (1). [From  $\bar{\text{C}}$  + benzenesulfonyl chloride in pyridine (1).]

③ 4,6-Dichloro-3-methylphenyl *p*-toluenesulfonate: very fine ndls. from alc., m.p. 104-105° (1). [From  $\bar{\text{C}}$  + *p*-toluenesulfonyl chloride in pyridine (1).]

3:1745 (1) Huston, Chen, *J. Am. Chem. Soc.* 55, 4216-4218 (1933). (2) von Walther, Zipper, *J. prakt. Chem.* (2) 91, 374 (1864). (3) Tanaka, Morikawa, Sakamoto, *J. Chem. Soc. Japan* 51, 275-277 (1930), *C.A.* 26, 706-707 (1932).

3:1754 6-CHLORO-3,4-DIMETHYLPHENOL  $\text{OH}$   $\text{C}_8\text{H}_9\text{OCl}$  *Beil.* VI —  
(5-Chloro-*o*-4-xylenol)  $\text{Cl}$   $\text{VI}_1$  —  
 $\text{VI}_2$ -(456)



M.P. 71.5-72.5° (1)  
72° (2)  
71° (4)

Ndis. from lt. pet. — Volatile with steam.

[For prepn. of  $\bar{C}$  from 6-amino-3,4-dimethylphenol (5-amino-o-4-xylene) [Beil. XIII-629, XIII-1-(244)] (1) via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reaction (yield not stated) see (1); from 3,4-dimethylphenol (o-4-xylene) (1:1453) with  $\text{SO}_2\text{Cl}_2$  in  $\text{CHCl}_3$  (23% yield) see (4) cf. (2) (3).]

[For studies on bactericidal action of  $\bar{C}$  see (2) (3).]

$\bar{C}$  with  $\text{Cl}_2$  does not (1) give a trichloro derivative.

$\bar{C}$  with  $\text{HNO}_3$  in  $\text{AcOH}$  soln. as directed gives (5) 2-nitro-6-chloro-3,4-dimethylphenol (5-chloro-3-nitro-o-4-xylene), yel. pl from  $\text{C}_6\text{H}_6$ , m.p.  $127.5^\circ$  (5); note, however, that neither the isomeric mononitro deriv. nor the corresp. dinitro deriv. is known.

$\bar{C}$  does not (5) couple with benzenediazonium chloride.

[For behavior of  $\bar{C}$  with sulfur chloride +  $\text{AlCl}_3$  in  $\text{CS}_2$  see (6).]

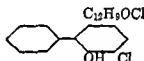
— 6-Chloro-3,4-dimethylphenyl acetate: unreported.

Ⓢ 6-Chloro-3,4-dimethylphenyl benzoate: m.p.  $43^\circ$  (1).

3:1754 (1) Hinkel, Collins, Ayling, *J. Chem. Soc.* 123, 2973 (1923) (2) Heicken, *Angew. Chem.* 52, 263-265 (1939). (3) Lockemann, Kunzmann, *Angew. Chem.* 46, 296-301 (1933). (4) McClement, Smiles, *J. Chem. Soc.* 1937, 1019 (5) Hinkel, Ayling, Bevan, *J. Chem. Soc.* 1928, 2530-2531. (6) Dvorkovitz, Smiles, *J. Chem. Soc.* 1938, 2026.

### 3:1757 6-CHLORO-2-PHENYLPHENOL

(3-Chloro-2-hydroxybiphenyl;  
"o-chloro-o'-phenylphenol")



Beil. S.N. 539

M.P. $73-74^\circ$ (1)	B.P. $313^\circ$	at 745 mm. (4)
$72^\circ$ (4)	$172^\circ$	at 15 mm. (4)
$71-72^\circ$ (3) (6)	$137-138^\circ$ at 5 mm.	(6)
	$138-140^\circ$ at 3 mm.	(10)

[See also 4-chloro-2-phenylphenol (3:8980).]

**Important Note.** Through the year 1944 (and perhaps in some cases beyond) the chloro-phenylphenol of m.p.  $72^\circ$  ( $\bar{C}$ ) has been regarded as having the structure 4-chloro-2-phenylphenol = 5-chloro-2-hydroxybiphenyl = "p-chloro-o-phenylphenol." In 1945, however, this view was corrected by the paper of Weissberger and Salminen (1); in this text, therefore, expression of the facts is reported in the light of their paper. Particular care is, therefore, required in consulting reference prior to it since such material is universally expressed in the reverse sense of the present view.

[For prepn. of  $\bar{C}$  from 2-hydroxybiphenyl (1:1440) with  $\text{Cl}_2$  (note that 4-chloro-2-phenylphenol (3:8980) is also formed) see (2) (4); for prepn. of  $\bar{C}$  from 3-amino-2-hydroxybiphenyl (5) by diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reaction (45% yield (1)) see indic. refs.]

$\bar{C}$  is sol. in aq. 25%  $\text{NaOH}$  at  $60^\circ$ , but resultant salt is more sol. than corresp. prod. from the isomeric 4-chloro-2-phenylphenol (3:8980) (for use in sepn. of  $\bar{C}$  from the latter see (4)); note that sodium salt of  $\bar{C}$  cryst. as trihydrate, i.e.,  $\text{Na}\bar{A}\cdot 3\text{H}_2\text{O}$  (4), and that anhydrous  $\text{Na}\bar{A}$  dec. at  $316^\circ$  without melting (4).

The calcium salt of  $\bar{C}$  is very spar. sol. aq. (use in sepn. of  $\bar{C}$  from the isomeric 4-chloro-2-phenylphenol (3)).

[For reaction of  $\bar{C}$  with methallyl chloride (3:7145) in pres. of alk. see (10).]

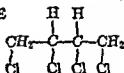
$\bar{C}$  on mononitration with  $\text{HNO}_3$  in  $\text{AcOH}$  at  $15-19^\circ$  as directed gives (31% yield (1)) 3-chloro-2-hydroxy-5-nitrobiphenyl, tan needles, m.p.  $130-131^\circ$  (1),  $129-131^\circ$  (6).

$\bar{C}$  (?) on condensation with formaldehyde + ethanolamine as directed (9) gives a prod., m.p.  $182-183^\circ$ ; for similar condens. of  $\bar{C}$  (?) with formaldehyde + morpholine see (7).]

— 6-Chloro-2-phenylphenyl benzoate: m.p.  $88.5^\circ$  (8). [Note that this prod. does not distinguish  $\bar{C}$  from the isomeric 4-chloro-2-phenylphenol (3:8980), whose benzoate has m.p.  $86-87^\circ$ .]

3:1757 (1) Weissberger, Salminen, *J. Am. Chem. Soc.* 67, 58-60 (1945). (2) Britton, Bryner (to Dow Chem. Co.), U.S. 1,969,963, Aug. 14, 1934; *C.A.* 28, 6160 (1934). (3) Rittler, Heller (to Chem. Fabrik von Heyden & Co.), U.S. 2,170,990, Aug. 29, 1939; *Cent.* 1939, II 4592; *C.A.* 34, 1098 (1940). (4) Britton, Bryner, *J. Am. Chem. Soc.* 67, 128-129; *C.A.* 27, 5086 (1935). (5) Vorozhts, *J. Am. Chem. Soc.* 56, 578 (1934). (6) Vorozhts, *J. Am. Chem. Soc.* 62, 1940, II 2162; *C.A.* 32, 790 (1939). (7) Coleman, Moore (to Dow Chem. Co.), U.S. 2,170,990, Aug. 29, 1939; *Cent.* 1939, II 4592; *C.A.* 34, 1098 (1940). (8) Bruosen, *J. Am. Chem. Soc.* 58, 1743 (1936). (9) Bruosen, *J. Am. Chem. Soc.* 58, 1743 (1936). (10) Coleman, Moore (to Dow Chem. Co.), U.S. 2,170,990, Aug. 29, 1939; *Cent.* 1939, II 4592; *C.A.* 34, 1098 (1940).

3:1760 1,2,3,4-TETRACHLOROBUTANE  
(solid isomer)  
(Butadiene tetrachloride;  
erythrene tetrachloride)



$\text{C}_4\text{H}_2\text{Cl}_4$  Beil. I - 119  
I<sub>1</sub>-(38)  
I<sub>2</sub>-

M.P.  $73-74^\circ$  (1) (2) B.P.  $130-134^\circ$  at 40 mm. (4)  
 $72.5-73^\circ$  (3)  
 $72^\circ$  (4)  
 $70^\circ$  (5)

This compd. is known in two diastereoisomeric forms, one solid ( $\bar{C}$ ), and one liquid (3:9082) q.v.

$\bar{C}$  cryst. from alc. (1) or  $\text{CCl}_4$  (3) in colorless pr. with strong camphoraceous odor.

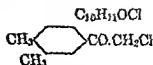
[For preparation of  $\bar{C}$  from butadiene-1,3 by treatment in cold with  $\text{Cl}_2$  (4) (6) (7) in  $\text{CS}_2$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , or lgr. soln. (4), or with  $\text{SCl}_2$  in pet. ether (1) see indic. refs.; for prepn. from 1,2,3,4-tetrahydroxybutane (erythritol) (1:5825) with  $\text{PCl}_5$  in  $\text{CS}_2$  see (3); for formn. from acetylene +  $\text{HCl}$  in electric discharge see (2).] [The proportion of solid ( $\bar{C}$ ) and liq. (3:9082) isomers formed varies with conditions.]

$\bar{C}$  on warming with Zn dust in alc. yields (4) butadiene-1,3, b.p.  $-4.8^\circ$ .

$\bar{C}$  with  $\text{MeOH/KOH}$  at  $10-18^\circ$  loses 2  $\text{HCl}$  yielding (8) 2,3-dichlorobutadiene-1,3 (3:5220), b.p.  $39-40^\circ$  at 80 mm., and other products.

3:1760 Backer, Strating, *Rec. trav. chim.* 54, 55-56 (1935). (2) Losanitch, *Cent.* 1913, II 754.

3:1775 3,4-DIMETHYLPHENACYL  
CHLORIDE  
( $\omega$ -Chloro-3,4-dimethyl-  
acetophenone)



Beil. VII - 323  
VII<sub>1</sub>-(172)

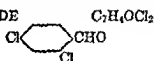
M.P. 73°

[For prepn. from *o*-xylene (1:7430) + chloroacetyl chloride (3:5235) +  $\text{AlCl}_3$  see (1) (2).]

$\bar{\text{C}}$  on oxidn. with alk.  $\text{KMnO}_4$  gives 4-methylisophthalic ac. [Beil. IX-863], m.p. 332° cor. (corresp. dimethyl ester, ndls. from MeOH, m.p. 80°).

3:1775 (1) Kuncell, *Ber.* 30, 1713 (1897). (2) Jörlander, *Ber.* 50, 1459 (1917).

3:1800 2,4-DICHLOROBENZALDEHYDE



Beil. VII - 230  
VII<sub>1</sub>-(134)

M.P. 74.5° (1)  
72° (2)  
71 (3) (5)  
70-71° (4)

White ndls. with strong odor like ordinary benzaldehyde. — Volatile with steam (1).

[For prepn. of  $\bar{\text{C}}$  from 2,4-dichlorotoluene (3:6290) via bromination at 180-200° to 2,4-dichlorobenzal (di)bromide and hydrolysis with conc.  $\text{H}_2\text{SO}_4$  at 100° (92% yield) see (1); for analogous prepn. via 2,4-dichlorobenzal (di)chloride and its hydrolysis see (2) (4); for prepn. of  $\bar{\text{C}}$  from 2-chloro-4-aminobenzaldehyde via diazo/ $\text{CuCl}$  reactn see (3).]

$\bar{\text{C}}$  on oxidn. with  $\text{KMnO}_4$  yields 2,4-dichlorobenzoic acid (3:4560), m.p. 162°. —  $\bar{\text{C}}$  on htg. with MeOH/ $\text{NaOMe}$  in s.t. at 183° for 8 hrs undergoes Cannizzaro reacto. yielding 2,4-dichlorobenzyl alc., m.p. 58-59° (2), and 2,4-dichlorobenzoic ac. (3:4560), m.p. 161-162° (2).

$\bar{\text{C}}$  on mononitration as specified (6) yields 2,4-dichloro-6-nitrobenzaldehyde [Beil. VII-263], cryst. from lgr., m.p. 74-75° (6). [Note that 2,4-dichloro-5-nitrobenzaldehyde [Beil. VII<sub>1</sub>-(144)], m.p. 74°, has also been prepd. indirectly.]

[For conversion of  $\bar{\text{C}}$  to 2,4-dichlorostyrene (7) (8) via reaction with  $\text{MoMgI}$  giving (63% yield (1)) 2,4-dichlorophenyl-methyl-carbinol, b.p. 130-134° at 11 mm. (1), 127° at 7 mm. (corresp. *p*-nitrobenzoate, m.p. 113° (1)), and dehydration of latter with  $\text{KHSO}_4$  (33% yield (7)) see indic. refs.]

① 2,4-Dichlorobenzaldoxime: ndls., m.p. 136-137° (4). [The oxime hydrochloride has m.p. 133.5° but on treatment with  $\text{Na}_2\text{CO}_3$  yields oxime (4).]

— 2,4-Dichlorobenzaldehyde phenylhydrazone: unrecorded.

— 2,4-Dichlorobenzaldehyde *p*-nitrophenylhydrazone: unrecorded.

— 2,4-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.

— 2,4-Dichlorobenzaldehyde semicarbazone: unrecorded.

3:1800 (1) Lock, Böck, *Ber.* 70, 923 (1937). (2) van der Lande, *Rec. trav. chim.* 51, 103, 109 (1932). (3) Blankens, *Chem. Weekblad* 6, 899-913 (1909), *Cent.* 1910, I 261. (4) Erdmann, Schwechten, *Ann.* 260, 68-69 (1890). (5) Seelig, *Ann.* 237, 169 (1887). (6) Geigy and Co., *Ger.* 198,909; *Cent.* 1908, II 214. (7) Marvel, Overberger, Allen, Johnston, Saunders, Young, *J. Am. Chem. Soc.* 68, 862-863 (1946). (8) Michalek, Clark, *Chem. & Eng. News* 22, 1559-1563 (1945).

3:1816 5-CHLORO-2-METHYLPHENOL  
(5-Chloro-o-cresol)

C<sub>7</sub>H<sub>7</sub>OCl

Beil. VI —

VI<sub>1</sub>-(174)VI<sub>2</sub>-(332)

M.P. 73-74° (1) (4)

Long white hard ndls. from pet. eth.; eas. sol. alc., AcOH; less sol. pet. eth. (1).

$\bar{C}$  is eas. sol. alk. (1).

[For prepn. from 5-chloro-2-methylaniline [Beil. XII-835] see (1) (4).]

$\bar{C}$  on mononitration (2) in AcOH with fuming HNO<sub>3</sub> at 5° gives mixt. of two mononitration products: 6-nitro-5-chloro-2-methylphenol, volatile with steam, golden-yel. pr. from pet. eth., m.p. 54.5-55° (2), and 4-nitro-5-chloro-2-methylphenol, not volatile with steam, cryst. from aq. or C<sub>6</sub>H<sub>6</sub>, m.p. 144-145° (2).

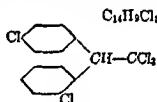
$\bar{C}$  on nitration (3) with 3 pts. HNO<sub>3</sub> (*D* = 1.48) at 0° gives a dinitro compd., 4,6-dinitro-5-chloro-2-methylphenol [Beil. VI<sub>1</sub>-(181)], yel. ndls., from pet. eth., m.p. 146° (3); acetyl deriv., m.p. 103-110° (3).

[For action of HNO<sub>3</sub> on  $\bar{C}$  see (4).]

⑥ 6-Chloro-2-methylphenyl benzoate: from  $\bar{C}$  + BzCl + aq. alk., white lfts. from alc., m.p. 53-54° (1).

3:1815 (1) Zincke, *Ann.* 417, 207-208 (1918). (2) von Auwers, Schornstein, *Cent.* 1924, II 2299. (3) Zincke, *Ann.* 418, 234 (1918). (4) Hodgson, Moore, *J. Chem. Soc.* 1926, 2037.

3:1820 1,1,1-TRICHLORO-2-(*o*-  
CHLOROPHENYL)-2-(*p*-  
CHLOROPHENYL)ETHANE  
(" *o,p'*-DDT")

C<sub>14</sub>H<sub>9</sub>Cl<sub>5</sub>

Beil. S.N. 479

M.P. 74.0-74.5° (4) cor. (6)

73-74° (5)

This compound is the so-called *o,p*-isomer of "DDT" (3:3298). Although known to be a substantial contaminant (e.g., 18% (1) —19% (5)) of technical "DDT," very little information is at present available regarding it.

Cryst. from MeOH.

[For prepn. of  $\bar{C}$  from 2,2,2-trichloro-1-(*o*-chlorophenyl)ethanol (5) with chlorobenzene (3:7903) in pres. of conc. H<sub>2</sub>SO<sub>4</sub> at 60° (64% yield) see (5).]

$\bar{C}$  on dinitration with fuming HNO<sub>3</sub> at 50° for 1 hr. gives (5) a dinitro deriv., cryst. from 95% alc., m.p. 148.0-148.5° cor. (5); note that this prod. has same m.p. as corresp. deriv. from "DDT" but that m.p. of a mixt. of the two dinitro compds. is depressed.

$\bar{C}$  on tetranitration with a mixt. (1:1 by volume) of fuming HNO<sub>3</sub> + conc. H<sub>2</sub>SO<sub>4</sub> at 100° for 1 hr. gives (2) a prod., m.p. 229.5-230° cor.; note that the corresp. prod. from "DDT" has m.p. 223.5-224.5° cor. (2).

$\bar{C}$  with anhydrous AlCl<sub>3</sub> (1 mole) + large excess C<sub>6</sub>H<sub>6</sub> at ord. temp. evolves HCl and gives (10% yield (3)) 1,1,2,2-tetraphenylethane, m.p. 211°; in this connection see corresp. behavior of "DDT" (3:3298).

$\bar{C}$  with alc. KOH loses 1 HCl giving (97% yield (5)) (7) 1,1-dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene (3:1925), accompanied by a little *o,p'*-dichlorodiphenylacetic acid, m.p. 106-107.5° cor. (7), the proportion of which may be increased by reaction of  $\bar{C}$  with Ba(OH)<sub>2</sub> in ethylene glycol at 175° (7).

3:1820 (1) Gunther, *J. Chem. Education* **22**, 239 (1945). (2) Schechter, Haller, *J. Am. Chem. Soc.* **66**, 2129-2130 (1944). (3) Fleck, Preston, Haller, *J. Am. Chem. Soc.* **67**, 1419-1420 (1945). (4) Cristol, Hayes, Haller, *Ind. Eng. Chem., Anal. Ed.* **17**, 470-473 (1945). (5) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1591-1602 (1945). (6) Cristol, *J. Am. Chem. Soc.* **67**, 1498 (1945). (7) Cristol, Haller, *J. Am. Chem. Soc.* **67**, 2222-2223 (1945).

3:1822 4-CHLORO-2,5-DIMETHYLPHENOL  
(5-Chloro-*p*-2-xylene)

 $C_8H_7OCl$ 

Beil. VI —

 VI<sub>1</sub>—

 VI<sub>2</sub>-(467)


M.P. 74-75° (1)

74° (2)

Nds. from lgr.

[For prepn. of  $\bar{C}$  from 2,5-dimethylphenol (*p*-xylene) (1:1473) by chlorination with  $SOCl_2$  in  $CHCl_3$  (1) or  $AcOH$  (2) see indic. refs.]

[For studies of bactericidal action of  $\bar{C}$  see (2) (3).]

[For behavior of  $\bar{C}$  with *o*-nitrosulfonyl chloride see (4) cf. (5); behavior of  $\bar{C}$  with sulfur chloride in  $CS_2$  see (1).]

— 4-Chloro-2,5-dimethylphenyl acetate: unreported.

— 4-Chloro-2,5-dimethylphenyl benzoate: unreported.

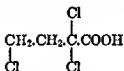
3:1823 (1) Lesser, Gad, *Ber.* **56**, 977 (1923). (2) Heicken, *Angew. Chem.* **52**, 264-265 (1939). (3) Lockemann, Kunzmann, *Angew. Chem.* **46**, 296-301 (1933). (4) Learmonth, Smiles, *J. Chem. Soc.* 1936, 327-328. (5) McClement, Smiles, *J. Chem. Soc.* 1937, 1010-1021.

3:1831  $\alpha,\alpha,\gamma$ -TRICHLORO-*n*-  
BUTYRIC ACID

 $C_4H_3O_2Cl_3$ 

Beil. II-281

 II<sub>1</sub>—

 II<sub>2</sub>—


M.P. 73-75° (1)

Cryst. with sharp odor suggesting chloroacetic acid. — Sol. in 20 pts. aq. —  $\bar{C}$  blisters skin. —  $\bar{C}$  in small amts. (5 g.) can (with care) be distilled, but attempts to distil larger units lead to decomposition with loss of  $HCl$  (2).

[For prepn. of  $\bar{C}$  from  $\alpha,\alpha,\gamma$ -trichloro-*n*-butyraldehyde (3:9094) by oxidn. with fung.  $HNO_3$  in cold see (1).]

$\bar{C}$  does not react with  $Zn$  dust in aq. or with aq.  $KI$  even at 100° (2);  $\bar{C}$  does not react with  $NH_2OH$  (2).

$\bar{C}$  on boilg. with aq. (100 pts.) for 4 days yields (2) a soln. which is strongly acid, reduces Fehling soln. and hot  $NH_4OH/AgNO_3$ , and presumably conts.  $HOCH_2CH_2CO.COOH$ .

$\bar{C}$  with aq.  $Na_2CO_3$  loses one of its three chlorine atoms (probably that in  $\gamma$  position) and upon acidification gives a soln. presumably contg. a lactone; for details see (2).

The acid chloride corresp. to  $\bar{C}$  is unreported.

— Methyl  $\alpha,\alpha,\gamma$ -trichloro-*n*-butyrate: unreported.

— Ethyl  $\alpha,\alpha,\gamma$ -trichloro-*n*-butyrate: unreported.

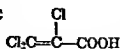
—  $\alpha,\alpha,\gamma$ -Trichloro-*n*-butyramide: unreported.

—  $\alpha,\alpha,\gamma$ -Trichloro-*n*-butyranilide: unreported.

—  $\alpha,\alpha,\gamma$ -Trichloro-*n*-butyr- $\alpha$ -naphthalide: unreported.

3:1831 (1) Natterer, *Monatsh.* **4**, 551-553 (1883). (2) Natterer, *Monatsh.* **5**, 258-265 (1884).



3:1840  $\alpha,\beta,\beta$ -TRICHLOROACRYLIC  
ACID $\text{C}_3\text{H}_2\text{O}_2\text{Cl}_3$ 
 Beil. II - 402  
 II<sub>1</sub>-(187)  
 II<sub>2</sub>-(388)

 M.P. 76° (1) (2) (13)  
 74-75° (3)  
 73° (4)  
 72.9° (5)

 B.P. 221-223° at 760 mm. (5)  
 133° cor. at 30 mm. (5)

Pr. from  $\text{CS}_2$  or dry ether. —  $\bar{\text{C}}$  is very eas. sol. hot aq. but spar. sol. cold aq.; at 25° its satd. aq. soln. conts. 6.4%  $\bar{\text{C}}$  (1), at 20° 6%  $\bar{\text{C}}$  (2). —  $\bar{\text{C}}$  with aq. within certain limits forms two liq. layers; for thermal anal. of the system see (5); note that  $\bar{\text{C}}$  with aq. forms a compd. of compn.  $\bar{\text{C}} + 2.5 \text{H}_2\text{O}$ , m.p.  $-0.6^\circ$ , and that  $\bar{\text{C}}$  with this compound forms a eutectic, m.p.  $17^\circ$  (5). —  $\bar{\text{C}}$  is very sol. in alc., ether, or  $\text{CHCl}_3$ .

[ $\bar{\text{C}}$  is usually prepd. from hexachloropropylene (3:6370) by direct or indirect hydrolysis of its terminal  $-\text{CCl}_2$  group to  $-\text{COOH}$ ; for prepn. of  $\bar{\text{C}}$  from hexachloropropylene by such hydrolysis with 90%  $\text{H}_2\text{SO}_4$  in pres. of  $\text{Al}_2(\text{SO}_4)_3$  at not above  $130^\circ$  (5) (1) cf. (6) (7) (81% yield (13)) or with boilg. aq. susp. of  $\text{BaCO}_3$  (isolated as  $\text{Ba}\bar{\text{A}}$  in 92% yield (1)) see indic. refs.; for prepn. of  $\bar{\text{C}}$  from hexachloropropylene (3:6370) via conversion with alc.  $\text{NaOEt}$  to triethyl orthotrichloroacrylate and subsequent quantitative hydrolysis with alc.  $\text{KOH}$  see (4).]

[For formn. of  $\bar{\text{C}}$  from hexachlorocyclopentanedione-1,3 [Beil. VII-553] by hydrolytic cleavage with 10%  $\text{NaOH}$  (3), or from  $\beta$ -bromo- $\alpha,\beta,\beta$ -trichloropropionic acid (see below) by elimination of  $\text{HBr}$  on stdg. several days with aq.  $\text{Ba}(\text{OH})_2$  (2), see indic. refs.]

$\bar{\text{C}}$  on reduction with  $\text{H}_2$  in pres. of  $\text{Pd}$  cat. at ord. temp. and press. absorbs 4 moles  $\text{H}_2$  yielding (8) propionic acid (1:1025).

$\bar{\text{C}}$  with  $\text{Cl}_2$  in  $\text{CCl}_4$  soln. in sunlight adds 1 mole halogen giving (9) (8) pentachloropropionic acid (3:4893).

[ $\bar{\text{C}}$  with  $\text{HBr}$  might be expected to yield  $\beta$ -bromo- $\alpha,\beta,\beta$ -trichloropropionic acid, but this reaction is unreported although the expected prod. [Beil. II-257], m.p.  $83-84^\circ$  has been prepd. by other means and with  $\text{Ba}(\text{OH})_2$  loses  $\text{HBr}$  giving  $\bar{\text{C}}$  (2).]

$\bar{\text{C}}$  with half its wt. of  $\text{PCl}_5$  at  $80^\circ$  loses  $\text{H}_2\text{O}$  between two molecules giving (4) trichloroacrylic acid anhydride, cryst., insol. aq., m.p.  $39-40^\circ$  (4) (5); this product is also formed during the distillation of  $\bar{\text{C}}$  even at reduced press. (5).

$\bar{\text{C}}$  with excess  $\text{SOCl}_2$ , however, gives (80-90% yield (1)) (13) trichloroacryloyl chloride (3:5845) q.v.

Salts of  $\bar{\text{C}}$ . [ $\text{Na}\bar{\text{A}}$  (conductivity of aq. solns.) (10);  $\text{K}\bar{\text{A}}$ , spar. sol. cold aq. (2);  $\text{Ag}\bar{\text{A}}$ , spar. sol. cold aq. but recryst. from hot aq. without decompn. (2) (4);  $\text{Mg}\bar{\text{A}}_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , sol. aq. (10);  $\text{Ca}\bar{\text{A}}_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , sol. aq. (10) (2);  $\text{Sr}\bar{\text{A}}_2 \cdot 5\text{H}_2\text{O}$ , sol. aq. (10);  $\text{Ba}\bar{\text{A}}_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , sol. aq. (10) (2) (note that this salt on htg. in atm. of  $\text{H}_2$  gives (11) dichloroacetylene (3:5010));  $\text{Zn}\bar{\text{A}}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Zn}\bar{\text{A}}_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$  (10);  $\text{Cd}\bar{\text{A}}_2 \cdot 2\text{H}_2\text{O}$  (10);  $\text{Hg}\bar{\text{A}}_2$  (no crystal aq.) (10).]

— Methyl  $\alpha,\beta,\beta$ -trichloroacrylate: unreported.

— Ethyl  $\alpha,\beta,\beta$ -trichloroacrylate: b.p.  $192-194^\circ$ ;  $112-114^\circ$  at 50 mm.;  $D_4^{20} = 1.2183$ ;  $n_D^{20} = 1.4649$  (4). [Prepd. indirectly from triethyl orthotrichloroacrylate (itself ohtd. from hexachloropropylene with  $\text{NaOEt}$ ) by shaking with conc.  $\text{HCl}$  (4).]

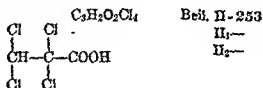
⑤  $\alpha,\beta,\beta$ -Trichloroacrylamide: m.p.  $97^\circ$  (12),  $96-97^\circ$  (4),  $96^\circ$  (2). [From trichloroacryloyl chloride (3:5845) with conc.  $\text{NH}_4\text{OH}$  (4) or from ethyl trichloroacrylate (above) with alc.  $\text{NH}_3$  (12).]

⑥  $\alpha,\beta,\beta$ -Trichloroacrylanilide: m.p.  $98^\circ$  (13). [From trichloroacryloyl chloride (3:5845) with aniline in  $\text{CHCl}_3$  at  $0^\circ$  (77% yield) (13).]

3:1840 (1) Böeseken, Dujardin, *Rec. trav. chim.* 32, 98-101 (1913). (2) Maberry, *Am. Chem. J.* 9, 3-6 (1887). (3) Zincke, Rohde, *Ann.* 239, 380 (1898). (4) Fritsch, *Ann.* 237, 315-318 (1897). (5) Böeseken, Carrière, *Rec. trav. chim.* 31, 179-186 (1915). (6) Prins, *J. prakt. Chem.* (2) 89, 416 (1914). (7) Prins, *Ger.* 261,689, July 2, 1913, *Cent.* 1913, II 394-395, *C.A.* 7, 3641 (1913). (8) Böeseken, van der Weide, *Rec. trav. chim.* 35, 272-273 (1927). (9) Böeseken, *Rec. trav. chim.* 46, 841 (1927). (10) Böeseken, *Rec. trav. chim.* 46, 844-845 (1927).

(11) Böeseken, Carrière, *Verslag Akad. Wetenschappen* 22, 1186-1188 (1914). (12) Gilta, *Bull. soc. chim. Belg.* 39, 587-588 (1930). (13) Bergmann, Haskelberg, *J. Am. Chem. Soc.* 63, 1438 (1941).

3:1850  $\alpha,\alpha,\beta,\beta$ -TETRACHLOROPROPIONIC ACID



M.P. 76° (1)

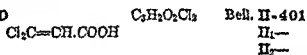
Colorless cryst. from  $\text{CS}_2 + \text{CHCl}_3$ ; fairly sol. aq.

[For prepn. of  $\bar{\text{C}}$  from  $\alpha,\beta$ -dichloroacrylic acid (3:2265) in  $\text{CS}_2$  with dry  $\text{Cl}_2$  in sunlight see (1).]

Salts:  $\text{K}\bar{\text{A}}$ ;  $\text{Ag}\bar{\text{A}}$  (readily dec. to  $\text{AgCl}$  on warming aq. soln.);  $\text{Ca}\bar{\text{A}}_2$ ;  $\text{Ba}\bar{\text{A}}_2$  (1).

3:1850 (1) Maberry, Smith, *Ber.* 22, 2059-2060 (1889).

3:1875  $\beta,\beta$ -DICHLOROACRYLIC ACID



M.P. 76-77° (1) (2) (3)

(Also see text.)

Ndls. from pet. ether or by sublimation. —  $\bar{\text{C}}$  is spar. sol. aq. but very eas. sol. ether or  $\text{CHCl}_3$ . —  $\bar{\text{C}}$  on htg. above its m.p. (e.g., to 120°), then rapidly cooled to 60° or below remelts at 63-64° (2) (3); on standing, however,  $\bar{\text{C}}$  finally reverts to the form of m.p. 76-77°.

—  $\bar{\text{C}}$  decomposes on attempted distn.

[For prepn. of  $\bar{\text{C}}$  from propiolic acid (acetylene-carboxylic acid) (Beil. II-477) by conversion to chloropropiolic acid (3:1685) and subsequent addn. of 1  $\text{HCl}$  by htg. with a large excess conc.  $\text{HCl}$  at 100° for 5 hrs. (77% overall yield from propiolic acid) see (1); for formn. from "chloralide" (3:3510) by reduction with  $\text{Zn} + \text{HCl}$  in alc. soln. see (2) (3).]

The behavior of  $\bar{\text{C}}$  toward hydrogenation has not been reported.

Neither  $\bar{\text{C}}$  nor its ethyl ester (see below) is stable to light.

[ $\bar{\text{C}}$  with  $\text{EtOH}$  gives  $\text{EtOOC}-\text{CH}=\text{CHCl}$  (3:3510) (1).]

the formn.

tion somet.

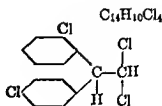
Salts:  $\text{K}\bar{\text{A}}$  (1);  $\text{Na}\bar{\text{A}}$  (2);  $\text{Ba}\bar{\text{A}}_2 \cdot 2\text{H}_2\text{O}$  (2);  $\text{Zn}\bar{\text{A}}_2 \cdot 2\text{H}_2\text{O}$  (3).

$\bar{\text{C}}$  with  $\text{PCl}_5$  gives (3)  $\beta,\beta$ -dichloroacryloyl chloride, b.p. above 145°; this prod. with  $\text{EtOH}$  or  $\bar{\text{C}}$  in  $\text{EtOH}$  with dry  $\text{HCl}$  gives (3) ethyl  $\beta,\beta$ -dichloroacrylate, b.p. 173-175°.

—  $\beta,\beta$ -Dichloroacrylamide: ndls. from  $\text{CHCl}_3$ , m.p. 112-113° (3). [From the above acid chloride with dry  $\text{NH}_3$  (3).]

3:1875 (1) Straus, Kollek, Herz, *Ber.* 63, 1876-1877 (1930). (2) Wallach, *Ann.* 203, 83-94 (1880). (3) Wallach, *Ann.* 193, 6-8, 19-28 (1875).

**3:1899 1,1-DICHLORO-2-(*o*-CHLOROPHENYL)-2-(*p*-CHLOROPHENYL)ETHANE**  
 (" *o,p*-DDD ")



Bell. S.N. 474

M.P. 76-78° (1)

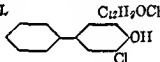
Colorless cryst. from MeOH or from pentane. — Note that  $\bar{C}$  is a minor impurity in technical grade "DDT" (3:3298).

[For prepn. of  $\bar{C}$  from 2,2-dichloro-1-(*o*-chlorophenyl)ethanol (1) with chlorobenzene (3:7903) in pres. of  $H_2SO_4$  (39% yield) see (1).]

$\bar{C}$  with alc. KOH loses 1 HCl giving (1) 1-chloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)-ethyleno (not described) which upon oxidn. with  $CrO_3/AcOH$  gives (1) 2,4-dichlorobenzophenone (3:1565).

3:1890 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1600 (1945).

**3:1899 2-CHLORO-4-PHENYLPHENOL**  
 (3-Chloro-4-hydroxybiphenyl)



Bell. S.N. 539

M.P. 77° (1) (4) B.P. 176.6° at 5 mm. (5)

$\bar{C}$  is sol. in NaOH. [For prepn. of  $Na\bar{A}$  using solns. of  $\bar{C}$  in org. solv. such as MeOH, ether, or toluene see (2).]

$\bar{C}$  htd. with NaOH/ $Na_2CO_3$  soln. under press. for 3 hrs. at 290-300° gives 4-phenylpyrocatechol [Bell. VI-990], m.p. 145°; diacetate, m.p. 77.5-78° (3).

$\bar{C}$  in  $CCl_4$  stood 5 days with 1 mole  $Br_2$  gave (44% yield) 6-bromo-2-chloro-4-phenylphenol, wh. pr. (from  $CHCl_3$ ), m.p. 84-86° cor. (4);  $\bar{C}$  in AcOH (25% yield) or in  $CS_2$  (56% yield) stood 2 days with 2 moles  $Br_2$  gave 6-bromo-4-(*p*-bromophenyl)-2-chlorophenol, coarse wh. ndls., m.p. 143-145° cor. (4).

$\bar{C}$  in AcOH treated with 1 mole  $HNO_3$  in AcOH gave 38% yield of 2-chloro-6-nitro-4-phenylphenol, thick yel. pl. (from  $CCl_4$ ), m.p. 89-90° cor. (5).

$\bar{C}$  with  $(CH_3)_2SO_4 + NaOH$  (1) or  $CH_3I + aq. KOH$  (5) yields the corresp. Me ether, 2-chloro-4-phenylanisole, m.p. 91-92° (1), 93° cor. (5).

① 2-Chloro-4-phenyl-phenyl acetate: m.p. 68° (7). [From  $\bar{C} + Ac_2O + NaOAc$  in 92% yield (7).]

② 2-Chloro-4-phenyl-phenyl benzoate: from  $\bar{C} + BzCl + aq. alk.$  in 80% yield (4); cryst. from AcOH (4), m.p. 95-97° cor. (4), 110-111° (6).

③ 2-Chloro-4-phenyl-phenyl benzenesulfonate: m.p. 59-60° (8). [From  $\bar{C} + benzenesulfonyl chloride + aq. 10\% NaOH$  (8).]

④ 2-Chloro-4-phenyl 2,4-dinitrophenyl ether: from  $\bar{C} + 2,4$ -dinitrochlorobenzene in conc. aq. KOH refluxed for several hrs.; yield, 70%; m.p. 109-111°C. (4).

U.S. 1,832,484, Nov. 17, 1931; *Cent.* 1932, I 740. (2)  
 Apr. 17, 1934; *Cent.* 1934, II 1991. (3) Harvey  
 27, 1934; *Cent.* 1934, II 1846. (4) Colbert, Meigs,  
 4). (5) Colbe  
*J. Am. Pha*

Savoy, Abernathy, *J. Am. Chem. Soc.* **64**, 2220 (1942).  
*Soc.* **64**, 2720 (1942).

3:1003  $\alpha,\beta$ -DICHLORO-*n*-BUTYRIC ACID (high-melting isomer) (Isocrotonic acid dichloride)  $\text{C}_4\text{H}_6\text{O}_2\text{Cl}_2$  Beil. II - 279  
 $\text{II}_1$ —  
 $\text{II}_2$ —

$$\text{CH}_3-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-\text{COOH}$$

M.P. 78° (1) (2) (5) B.P. 131.5° at 20 mm. (2)  
 72-73° (3) (4) 130-131° at 18 mm. (5)

[See also  $\alpha,\beta$ -dichloro-*n*-butyric acid (low-melting isomer) (crotonic acid dichloride) (3:1375).]

Colorless cryst. from pct. ether. —  $\bar{\text{C}}$  is very eas. sol. alc., ether, much less sol. aq.

[For prepn. of  $\bar{\text{C}}$  from  $\alpha$ -chlorocrotonic acid (3:2760) by addn. of 1 HCl using conc. aq. HCl (satd. at 0°) in s.t. at 100° for 50 hrs. see (2) (4); from either  $\alpha$ -chloro- $\beta$ -hydroxy-*n*-butyric acid of m.p. 62° [Beil. III-309] (4) or from  $\beta$ -chloro- $\alpha$ -hydroxy-*n*-butyric acid of m.p. 125° [Beil. III-306] (3) by htg with conc. aq. HCl (satd. at 0°) in s.t. at 100° for 40 hrs. see indic. refs.; for formn. of  $\bar{\text{C}}$  by (partial) isomerization of the lower-melting isomer (crotonic acid dichloride) (3:1375) with conc HCl in s.t. at 100° see (5); from the amide (see below) corresp. to  $\bar{\text{C}}$  with  $\text{HNO}_2$  see (1) ]

$\bar{\text{C}}$  behaves as an acid but is slightly weaker than its isomer; ionization const. of  $\bar{\text{C}}$  is  $61 \times 10^{-3}$  (5); its reported salts include  $\text{Ag}\bar{\text{A}}$ , spar. sol. aq. (4),  $\text{Ba}\bar{\text{A}}_2 \cdot 3\text{H}_2\text{O}$  (4); and  $\text{Zn}\bar{\text{A}}_2$  (4).

$\bar{\text{C}}$  with alc. KOH loses 1 mole HCl giving (2) (4) mainly  $\alpha$ -chlorocrotonic acid (3:2760) accompanied by some  $\alpha$ -chloro-isocrotonic acid (3:1615).

The acid chloride corresp. to  $\bar{\text{C}}$  is unreported.

— Methyl  $\alpha,\beta$ -dichloro-*n*-butyrate: unreported.

— Ethyl  $\alpha,\beta$ -dichloro-*n*-butyrate: unreported.

—  $\alpha,\beta$ -Dichloro-*n*-butyramide: m.p. 125° (1). [Prepd. indirectly but with  $\text{HNO}_2$  gives  $\bar{\text{C}}$  (1).]

3:1903 (1) Rambaud, *Bull. soc. chim.* (5) 1, 1339 (1934). (2) Michael, Schulthess, *J. prakt. Chem.* (2) 46, 259-262 (1892). (3) Melikoff, Petrenko-Kritschenko, *Ann.* 266, 371-374 (1891). (4) Melikoff, *Ann.* 234, 201-204 (1886). (5) Michael, Bunge, *Ber.* 41, 2911 (1908).

3:1905  $\alpha,\beta,\gamma$ -TRICHLORO-*n*-BUTYRALDEHYDE HYDRATE  $\text{C}_4\text{H}_7\text{O}_2\text{Cl}_3$  Beil. I - 664  
 $\text{I}_1$ —  
 $\text{I}_2$ -(725)

$$\text{CH}_3-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{CH}}}-\overset{\text{Cl}}{\underset{\text{OH}}{\text{C}}}-\text{CH}_2\text{OH}$$

M.P. 78° (1)  
 77-78° (2)  
 77° (24)  
 74-74.5° (3)

[See also  $\alpha,\beta,\gamma$ -trichloro-*n*-butyraldehyde (butyrylchloral) (3:5910).]

Lfts. from aq. or alc. — Spar. sol. cold but fairly eas. sol. hot aq.; very eas. sol. alc. — For crystallographic data see (3) (5). — Note that because of tendency to dissociate on htg. into butyrylchloral (3:5910) + aq. the ro.p. observed for  $\bar{\text{C}}$  varies according to rate of htg. (3). — Note also that  $\bar{\text{C}}$  is isomeric with chloral ethylalcoholate (3:0860) with which it must not be confused; for distinction of  $\bar{\text{C}}$  from chloral hydrate (3:1270) see (9) (10).

$\bar{\text{C}}$  is employed in medicine as a sedative; from the body it is excreted in the urine as urobutyrylchlorallic acid [Beil. I-664], which upon hydrolysis yields (4) 2,2,3-trichlorobutanol-1 (3:1336) + glucuronic acid [Beil. III-884, III-(306)].

[For prepn. of  $\bar{C}$  from butyrylchloral (3:5910) by reactn. with aq. see (1) (2) (6).]

[ $\bar{C}$  is reduced by fermenting yeast giving (7) dextrorotatory 2,2,3-trichlorobutanol-1, m.p. 62°; for actn. of  $\bar{C}$  on alc. fermentation see (8).]

$\bar{C}$  on oxidn. with 3 wt. pts. fung.  $\text{HNO}_3$  ( $D = 1.504$ ) nt 30–35° for 1½ hrs. then stood at room temp. for 24 hrs. gives (95% yield (11))  $\alpha,\alpha,\beta$ -trichloro-*n*-butyric acid (3:1280).

$\bar{C}$  on distn. with half its wt. of  $\text{Ac}_2\text{O}$  (12), or shaking with conc.  $\text{H}_2\text{SO}_4$  (13), or on distn. with  $\text{CHCl}_3$  (14), or on htg. alone loses its combined aq. yielding butyrylchloral (3:5910), h.p. 165°.

$\bar{C}$  with conc.  $\text{H}_2\text{SO}_4$  (at least 6 wt. pts.) nt room temp. for 2 days trimerizes to a mixt. (80% yield (12)) of two parahutyrylchlorals: these are colorless crystn., sharp-melting solids, sol. in org. solvents, but insol. nq.; the less sol.  $\alpha$ -parahutyrylchloral, rhombic cryst. from boilg.  $\text{AcOH}$  or boilg.  $\text{EtOH}$ , has m.p. 180°; the more sol.  $\beta$ -parahutyrylchloral (stereoisomer?), cryst. from boilg.  $\text{AcOH}$  or boilg.  $\text{EtOH}$ , has m.p. 157°; these polymers can be distilled at 15 mm. but attempts to distil them at ord. press. result in complete dissociation to butyrylchloral (3:5910).

$\bar{C}$  with aq.  $\text{KOH}$  or  $\text{NaOH}$  evolves heat and yields (1) (15) 1,1-dichloropropene-1 (3:5120) + the salt of formic acid (1:1005).

[ $\bar{C}$  with conc. nq.  $\text{HCN}$  fails (16) to react, but upon addn. of alc. and subsequent digestion (15), or  $\bar{C}$  (1 mole) with aq.  $\text{KCN}$  (2 moles) at 40° (17), gives (20% yield (17))  $\alpha,\alpha,\beta$ -trichloro-*n*-butyraldehyde cyanohydrin [Beil. III-322, III<sub>2</sub>-(226)], pl. from aq., m.p. 101–102° (17) (18), accompanied by (61% yield (17))  $\alpha$ -chlorocrotonic acid (3:2760), m.p. 98.5–99° (17). — Note that  $\bar{C}$  (1 mole) in alc. treated gradually with powdered  $\text{KCN}$  (2 moles) below 15° over a 3–4 hr. period gives (90% yield (17)) ethyl  $\alpha$ -chlorocrotonate (3:8523); in this reactn. the intermediate ethyl  $\alpha,\beta$ -dichloro-*n*-butyrate readily loses  $\text{HCl}$  and is generally not isolated; use of alcs. other than  $\text{EtOH}$  gives good yields of the corresp. alkyl  $\alpha$ -chlorocrotonates (17). — Note that for  $\bar{C}$  with  $\text{KCN}$  in  $\text{C}_6\text{H}_6$  the reaction takes a different course (17). — Finally, note that  $\bar{C}$  (1 mole) in conc. aq.  $\text{NH}_4\text{OH}$  first dissolves, then ppts. butyrylchloral-ammonia as a heavy oil; the mixt. on sata. with dry  $\text{NH}_3$  gas in cold followed by treatment at 10° with powdered  $\text{KCN}$  (1 mole) evolves heat and gives (93% yield (17))  $\alpha$ -chlorocrotonamide, m.p. 113.5° (17).]

[ $\bar{C}$  undergoes cocondensation with various org. systems: e.g.,  $\bar{C}$  with phenyl isocyanide (1 mole) in ether for 4–5 days gives (53% yield (19))  $\alpha$ -hydroxy- $\beta,\beta,\gamma$ -trichloro-valerianilide, thls. from alc.,  $\text{C}_6\text{H}_6$ , or  $\text{CHCl}_3$ , m.p. 156–158° (19). —  $\bar{C}$  (1 pt.) with malonic acid (1:0480) (1 pt.) in pyridine (1 pt.) at 100° for 3 hrs. evolves  $\text{CO}_2$  and gives (20)  $\beta$ -hydroxy- $\gamma,\gamma,\delta$ -trichloro-*n*-caproic acid, cryst. from hot aq., m.p. 102° (20). —  $\bar{C}$  (1 mole) with nitromethane (1½ moles) in dil. alc. in pres. of  $\text{Na}_2\text{SO}_3$  nt 60° gives (100% yield (21)) 1-nitro-3,3,4-trichloropentanol-2, h.p. 156° at 4 mm., m.p. abt. 20° (21);  $\bar{C}$  (1 mole) with nitroethane (1 mole) in 50% alc. in pres. of  $\text{Na}_2\text{SO}_3 + \text{K}_2\text{CO}_3$  nt 70° gives (22) 2-nitro-4,4,5-trichlorohexanol-3, h.p. 138° nt 0.75 mm. (22).]

[ $\bar{C}$  forms with various org. substances molecular cpds. of pharmaceutical interest: e.g.,  $\bar{C}$  (1 mole) with quinine (base) (1 mole) in abs. alc. at 75° for 1 hr. gives 1:1 cpd., m.p. 139° (note that the corresp. cpd. from chloral (3:5210) + quinine has m.p. 149° (23)). —  $\bar{C}$  (1 mole) with 2,3-dimethyl-1-phenylpyrazolone-5 ("Antipyrine") (1 mole) (m.p. 112°) rubbed together and recrystd. from aq. gives (24) 1:1 molecular cpd., colorless pr., m.p. 72° (for f.p./compn. data and diagram of this system see (24)). —  $\bar{C}$  with 2,3-dimethyl-4-dimethylamino-1-phenylpyrazolone-5 ("Pyramidone") (m.p. 107.5°) on fusion or in aq. or  $\text{C}_6\text{H}_6$  (24) (25) (26) gives a 1:1 mol. cpd. ("Trigemin"), cryst. from  $\text{C}_6\text{H}_6$ , m.p. 85–86° (26), long ndls. from aq., m.p. 84° (24) (for f.p./compn. data and diagram on this system see (24)); for stabilization of "Trigemin" by addn. of 5–10% hexamethylenetetramine (27) or 2%  $\text{MgO}$  (28) see indic. refs.]

[ $\bar{C}$  with various org. hydroxy acids in pres. of conc.  $H_2SO_4$  condenses to give prods. of the chloralide type: e.g., for reactn. of  $\bar{C}$  with citric acid (1:0505), malic acid (1:0450), or tartaric acid (1:0525) see (29); with gallic acid (1:0875) (and numerous other phenolic acids) see (30).]

$\bar{C}$  with conc. aq.  $NH_4OH$  first dissolves then ppts. a heavy oil of butyrylchloral-ammonia (17); cryst. m.p.  $62^\circ$  (see also above for its reaction with KCN).

[ $\bar{C}$  with excess dry  $NH_4OAc$  on moderate hgt for several hrs, then pouring into aq., gives (18)  $\alpha, \beta$ -trichloro-*n*-butyraldimine, cryst from  $C_6H_6$ , m.p.  $169-170^\circ$  (31),  $164-165^\circ$  (18); observe that this m.p. is notably close to that of the condensation prod. of butyrylchloral (3:5910) with acetamide, and that latter is readily formed from  $NH_4OAc$  by dry hgt.; this matter, however, seems to have received no further attention.]

$\bar{C}$  with aq.  $NH_2OH.HCl$  on hgt. readily yields (32)  $\alpha, \beta$ -trichloro-*n*-butyraldoxime (first separating as an oil), cryst. from lgr, m.p.  $65^\circ$  (32)

The reaction of  $\bar{C}$  with arylhydrazines is of special interest and has been extensively studied. With phenylhydrazine the reaction is extremely vigorous (33) (34) and unless carefully controlled (35) may become almost explosively violent yielding only tar. With nuclear-substituted phenylhydrazines, however, the reaction is milder, and their study has shown that all arylhydrazines react in the same general pattern although this comprises several different courses according to the solvent used. The pattern will be illustrated here only by the case of 2,4-dichlorophenylhydrazine (see below); for details of the analogous reaction of  $\bar{C}$  with phenylhydrazine (33) (34), *o*-, *m*-, and *p*-tolylhydrazines (34), 2,5-dichlorophenylhydrazine (35) (36), 3,5-dichlorophenylhydrazine (35), 2,4,5-trichlorophenylhydrazine (36), 2,4,6-trichlorophenylhydrazine (36), *p*-bromophenylhydrazine (34), 2,4-dibromophenylhydrazine (37), 4,5-dibromophenylhydrazine (35), and 2,4,6-tribromophenylhydrazine (35) see indic. refs.

[The reactn. of  $\bar{C}$  (1 mole) with 2,4-dichlorophenylhydrazine hydrochloride (1 mole) first gives the expected butyrylchloral 2,4-dichlorophenylhydrazone (A) which, however, cannot be isolated because of immediate further reaction in two different modes according to the solvent employed. In dil aq.  $HCl$  contg.  $NaOAc$  (A) loses  $HCl$  in two different ways leading on one hand to  $\alpha, \beta$ -dichloroacetaldehyde 2,4-dichlorophenylhydrazone (B), long yel. pr. from alc. or  $AcOH$ , m.p.  $112^\circ$  (34), and on the other (simultaneously and with rearr. of unsatd. linkages) to the crimson 1-(2,4-dichlorobenzeneazo)-2,3-dichlorobutene-1 (C) (in most instances the last is not isolatable in pure form although it has been in the case (37) of  $\bar{C}$  with 2,4-dibromophenylhydrazine), in  $MeOH$ ,  $EtOH$ , or  $AcOH$ , however, the two  $\alpha$ -chlorine atoms of the initial arylhydrazone (A) undergo hydrolysis with consequent formn. of  $\beta$ -chloro- $\alpha$ -keto-*n*-butyraldehyde 2,4-dichlorophenylhydrazone (D), pale yel. pr. from alc., m.p.  $129^\circ$  (33)]

[This last type of epl. (D) can be caused to undergo two further important types of reaction: e.g., (D) with further 2,4-dichlorophenylhydrazine in  $MeOH$  soln. not only undergoes conventional condensation of its  $\alpha$ -keto grouping but also has the  $\beta$ -chlorine atom replaced by methoxyl so that the product obt'd is  $\beta$ -methoxy- $\alpha$ -keto-*n*-butyraldehyde bis-(2,4-dichlorophenyl)oxazone (E), bright yel. pr. from pyridine or  $C_6H_6$ , m.p.  $196^\circ$  dec. (33) (this reaction occurs so readily in  $MeOH$  that from  $\bar{C}$  + 2,4-dichlorophenylhydrazine hydrochloride both (D) and (E) are formed and may be separated by fractional crystn.); on the other hand, (D) with alc.  $NaOEt$  on hgt. loses  $HCl$  and ring-closes (38) to 1-(2,4-dichlorophenyl)-4-hydroxy-5-methylpyrazole (F), colorless cryst. from boilg. alc., m.p.  $144^\circ$  (35) (this type of reactn. comprises a general synthesis of 4-hydroxypyrazoles).]

3:190: (1) Kramer, Pinner, *Ber.* 3, 383 390 (1870). (2) Mourou, Murat, Tampier, *Bull. soc. chim.* (4) 29, 33 (1921). (3) Lieben, *Zeitsch. Monatsch.* 4, 534 538 (1883). (4) Meiring, *Z. physiol. Chem.* 8, 471-476 (1882). (5) von Lang, *Z. Krist.* 23, 521-522 (1896). (6) Pinner, *Ann.* 179,

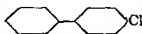


$\bar{C}$  with 1 mole aniline on htg. at 180-190° for 2 hrs. (1), or indirectly from *m*-chlorobenzyl phenyl ketoxime by Beckmann rearr. with  $\text{PCl}_5$  in ether (64-82% yield (1)).]

- ① (3-Chlorophenylacet)-*m*-chloroanilide: white ndls. from dil. alc., m.p. 120° cor. (1). [From  $\bar{C}$  with *m*-chloroaniline (1 mole) on htg. at 180-190° for 2 hrs (1), or indirectly from *m*-chlorobenzyl *m*-chlorophenyl ketoxime by Beckmann rearr. with  $\text{PCl}_5$  in ether (64-82% yield (1))]

3:1910 (1) Jenkins, *J. Am. Chem. Soc.* 55, 2898-2899 (1933). (2) Kenner, Morton, *J. Chem. Soc.* 1934, 679-680. (3) Dippy, Williams, *J. Chem. Soc.* 1934, 1888-1892. (4) Buck, Ide, *J. Am. Chem. Soc.* 54, 3307-3309 (1932). (5) Muenzen, Cerecedo, Sherwin, *J. Biol. Chem.* 68, 508-510 (1920). (6) Ivanov, Pchnénitchny, *Bull. soc. chim.* (5) 1, 231-232 (1934).

3:1912 4-CHLOROBIPHENYL  
(4-Chloro-xenene (15))



$\text{C}_{12}\text{H}_9\text{Cl}$

Beil. V - 579

$\text{V}_1$ —

$\text{V}_2$ -(483)

M.P. 77.7°	(1)	B.P. 291.2°	at 745 mm. (5)
77.5°	(2) (3)	282°	(12)
77.2-77.4°	(4)	222-226°	at 150 mm. (14)
77.2°	(5)		
77°	(6) (7) (8)		
76°	(9) (10) (21) (25)		
75.5°	(11) (12)		
75-76°	(13)		

Colorless cryst. from alc. (0.8 ml./g. (5)); somewhat less sol. in alc. than isomeric 2-chlorobiphenyl (3:0300). — Volatile with steam. — [For f.p./compn. curves of systems:  $\bar{C}$  + biphenyl (1:7175),  $\bar{C}$  + 4-fluorobiphenyl, or  $\bar{C}$  + 4-bromobiphenyl, see (7)]

[For prepn. of  $\bar{C}$  from biphenyl (1:7175) with  $\text{Cl}_2$  in pres. of Fe (30% yield (5)) (14) (16) (17), or  $\text{SbCl}_5$  (12), see indic. refs. (2-chlorobiphenyl (3:0300) is also formed; for use of mixt. for transformer oil see (18); for sepn. of mixt. see (10)); for prepn. of  $\bar{C}$  from *p*-aminobiphenyl via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reactn. see (2) (7).]

[For prepn. of  $\bar{C}$  from *p*-chloroaniline [Beil. XII-607, XII-(604)] via diazotization and coupling of resultant diazonium salt with  $\text{C}_6\text{H}_6$  in aq. NaOH suspension (yields: 41% (1), 40% (6)) cf. (21) (23) or in aq. NaOAc (yield = 35% (6)), or by formn. of *p*-chlorobenzene-diazonium chloride/ $\text{ZnCl}_2$  epd. and reactn. of latter with  $\text{C}_6\text{H}_6$  in AcOH + NaOAc (yield = 34% (20)) see indic. refs.: from *N*-nitroso-aect-*p*-chloroanilide with  $\text{C}_6\text{H}_6$  in  $\text{CHCl}_3$  for a few days at room temp. see (13).]

[For formn. of  $\bar{C}$  from decompn. of dibenzoyl peroxide (1:4930) in boilg. chlorobenzene see (22); from decompn. of benzoyl *p*-chlorobenzoyl peroxide see (23); from di-(*p*-chlorobenzoyl) peroxide in  $\text{C}_6\text{H}_6$  see (24) (4) (3); for formn. of  $\bar{C}$  from 4-hydroxybiphenyl (1:1585) with  $\text{PCl}_5$  see (10); from *p*-xenylselenium trichloride on htg. see (25); from *p*-chloriodobenzene + Cu powder see (2)]

[ $\bar{C}$  with aq. 15-30% NaOH at 300-400° under pressure (26) in pres. of Cu (27), or  $\bar{C}$  with aq.  $\text{Na}_2\text{CO}_3$  + Cu at 300° (28), or  $\bar{C}$  with aq. vapor over cat. at 525-600° (29) gives (75% yield (26)) 4-hydroxybiphenyl (1:1585) (28) (29) or its mixt. with 3-hydroxybiphenyl (1:1475) (27).]

[ $\bar{C}$  with conc. aq.  $\text{NH}_4\text{OH}$  + cat. under press. as directed (30) (31) gives *p*-aminobiphenyl]

[ $\bar{C}$  with Li in dry ether under  $\text{N}_2$  gives (32) Li *p*-xenyl. —  $\bar{C}$  with Na sand in  $\text{C}_6\text{H}_6$  at 110-120° under press. followed by carbonation with  $\text{CO}_2$  gives (65-67% yield (33)) biphenyl-4-carboxylic acid (*p*-phenylbenzoic acid) [Beil. IX-671, IX-(280)]. —  $\bar{C}$  with Na



+ diethyl carbonate (1:3150) in  $C_6H_6$  as directed gives (yields: 42% (35), 35-40% (36), 39% (37), 23% (38)) tri-(*p*-xenyl)carbinol (*tris-p*-biphenylcarbinol) [Beil. VI-738, VI-(369)], colorless cryst. from AcOH, m.p. 207-208° (36), 207° (38), 206-207° (37). —  $\bar{C}$  with Na + benzophenone (1:5150) in  $C_6H_6$  gives (67% yield (34)) diphenyl-*p*-xenylcarbinol [Beil. VI-732], colorless cryst. from lgr., stable form, m.p. 135-136° (34), metastable form, m.p. 112-113° (34).]

[For reactn. of  $\bar{C}$  with Na +  $AsCl_3$  giving (39) tri-(*p*-xenyl)arsine, with Na +  $SbCl_3$  giving (40) tri-(*p*-xenyl)stibine, with Na +  $PCl_3$  giving (41) tri-(*p*-xenyl)phosphine, or with Na +  $SiCl_4$  giving (42) tetra-(*p*-xenyl)silane see indic. refs.]

[ $\bar{C}$  + stearoyl chloride (3:9960) +  $AlCl_3$  in  $CS_2$  gives (43) heptadecyl *p*-chloroxenyl ketone, m.p. 96-97° (43). —  $\bar{C}$  + cyclohexene (1:8070) +  $AlCl_3$  gives (44) a mixt. of cyclohexyl-*p*-chlorobiphenyls.]

[ $\bar{C}$  + phthalic anhydride (1:0725) +  $AlCl_3$  as directed (45) (46) gives (93% yield (45)) *o*-[4-(*p*-chlorophenyl)benzoyl]benzoic acid, colorless rods from AcOH or toluene, m.p. 251° cor. (45), 249.6-250.6° (46).]

The nitration of  $\bar{C}$  does not appear to have been reported.

$\bar{C}$  on oxidn. with  $CrO_3$  in AcOH yields (10) (25) *p*-chlorobenzoic acid (3:4940), m.p. 237° (10) (25).

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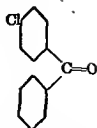
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Aug. 14, 1934; *Cent.* 1935,  
as, U.S. 1,786,526, 1,786,

3:1914 4-CHLOROBENZOPHENONE  
(*p*-Chlorophenyl phenyl  
ketone)

C<sub>13</sub>H<sub>9</sub>OClBeil. VII - 419  
VII<sub>1</sub>-(227)

M.P. 78.4° (1)  
78° (28)  
77-78° (2)  
76-77° (35)  
76° (3) (4)  
75.5-76° (5) (37)  
75-77° (6)  
75° (7)  
72-73° (8)

B.P. 332° at 771 mm. (7)  
322-325° (8)

Colorless ndls. from alc., 80% alc., or ether + alc. — Eas. sol. hot alc. but spar. sol. cold alc., eas. sol. ether, spar. sol. cold lgr. (For search for possible polymorphic forms see (4) (9) (10).]

[For prepn. of  $\bar{C}$  from benzoic acid (1:0715) + chlorobenzene (3:7903) with AlCl<sub>3</sub> (82.4% yield  $\bar{C}$  + 11.9% 2-chlorobenzophenone (3:0715) (1)), or with P<sub>2</sub>O<sub>5</sub> at 180-200° (5), see indic. refs.; from benzoyl chloride (3:6240) + chlorobenzene (3:7903) with AlCl<sub>3</sub> (yields: 97% (37), 86% (8), 80-90% (7) (11), 45% (4), 40% (2)) (3) (some 2-chloro isomer also being formed (12)) see indic. refs.; from *p*-chlorobenzoyl chloride (3:6550) + benzene with AlCl<sub>3</sub> (84.6% yield) see (6); from tetra-(4-chlorophenyl)ethylene glycol *bis*-(magnesium iodide) in quant. yield with I<sub>2</sub> or O<sub>2</sub> see (13); from *p*-chlorobenzohydrylidene- $\alpha$ -phenylethylamine by hydrol. with warm dil. H<sub>2</sub>SO<sub>4</sub> see (8).]

[ $\bar{C}$  on reduction with Al/Hg in 80% alc. (3) (14) or with 3% Na/Hg (7) or on boilg. with alc. KOH for 2 days (15), or exposure to sunlight for 7 days of its soln. in isopropyl alc. contg. Na isopropylate, gives (85% yield (3) (14), 80% yield (16)) 4-chlorophenyl-phenyl-carbinol (4-chlorobenzohydrol) [Beil. VI-680, VI<sub>1</sub>-(327)], m.p. 67.5° (3) (14), 62° (7), accompanied by a little (14% (3) (14))  $\alpha,\alpha'$ -diphenyl- $\alpha,\alpha'$ -bis-(4-chlorophenyl)ethylene glycol (*sym*-4,4'-dichlorobenzopinacol) [Beil. VI<sub>1</sub>-(523)], m.p. 179° (3) (14). —  $\bar{C}$  with Zn + AcOH yields 4-chlorobenzohydryl acetate (12) or a mixt. (7) of 4-chlorobenzohydrol (above) + the corresp. pinacol (see below).]

[ $\bar{C}$  with Mg + MgI<sub>2</sub> in ether + C<sub>6</sub>H<sub>6</sub> or  $\bar{C}$  in very dil. alc. soln. in sunlight (7) gives (94% yield (13)) *sym*-4,4'-dichlorobenzopinacol, m.p. 172-178° (see above). —  $\bar{C}$  with Zn dust + H<sub>2</sub>SO<sub>4</sub> in nq. AcOH yields (12) *sym*-4,4'-dichloro- $\alpha$ -benzopinacolone (*sym*-4,4'-dichlorotetraphenylethylene oxide) [Beil. XVII<sub>1</sub>-(45)], ndls. from AcOH, m.p. 220° dec. (12). — For oxidn.-reductn. potential of  $\bar{C}$  see (35)]

[ $\bar{C}$  with conc. H<sub>1</sub> + red P in AcOH refluxed 14 hrs. gives (7) 4-chlorodiphenylmethane [Beil. V-590, V<sub>1</sub>-(278), V<sub>2</sub>-(500)], b.p. 298° at 742.5 mm. (7).]

[ $\bar{C}$  with diphenylmethyl sodium (benzohydryl-sodium) followed by aq. gives (18) corresp. tertiary alc., viz., benzohydryl-*p*-chlorophenyl-phenyl-carbinol, m.p. 176-178° (18), which with acetyl chloride loses H<sub>2</sub>O to give 4-chlorotetraphenylethylene [Beil. V<sub>1</sub>-(376), V<sub>2</sub>-(679)], m.p. 166-167° (18). —  $\bar{C}$  with MeMgI in dry ether yields (19) *p*-chlorophenyl-phenyl-methyl-carbinol which on loss of aq. by htg. as directed gives (66% overall yield)  $\alpha$ -(4-chlorophenyl)- $\alpha$ -phenylethylene, b.p. 164° at 16 mm. (19); note that this prod. with

$\text{Br}_2$  does not add halogen but rather evolves  $\text{HBr}$  yielding (20) both solid (m.p. 94–95°) and liq. stereoisomers of  $\beta$ -(4-chlorophenyl)- $\beta$ -phenylvinyl bromide. —  $\bar{\text{C}}$  with  $\beta$ -(4-chlorophenyl)- $\beta$ -phenylvinyl  $\text{MgBr}$  as directed (23) gives 1,4-di-(*p*-chlorophenyl)-1,4-diphenylbutadiene-1,3, yellowish green ndls. from amyl alc., m.p. 230° (23). —  $\bar{\text{C}}$  with triphenylmethyl  $\text{MgBr}$  in ether +  $\text{C}_6\text{H}_6$ , followed by dil.  $\text{AcOH}$ , gives (21) 78% yield *sym*-4,4-dichlorohenzopinacol (see above) + 80% yield triphenylmethyl peroxide.]

[ $\bar{\text{C}}$  with ethyl bromoacetate +  $\text{Zn}$  in dry  $\text{C}_6\text{H}_6$  gives (yields: 79% (22), 67% (24)) ethyl  $\beta$ -(4-chlorophenyl)- $\beta$ -hydroxy- $\beta$ -phenyl-propionate, m.p. 79–80.5° (22), 69° (24); this prod. on htg. with 85% formic acid gives (66% yield (24)) ethyl  $\beta$ -(4-chlorophenyl)cinnamate, h.p. 210–212° at 13 mm. (24), or on hydrolysis gives (22)  $\beta$ -(4-chlorophenyl)- $\beta$ -hydroxy- $\beta$ -phenylpropionic acid, m.p. 188.5–189° dec. (22).]

$\bar{\text{C}}$  with  $\text{PCl}_5$  at 150° gives (yields: 90% (25) (27), 88% (26) (8))  $\alpha,\alpha$ -4-trichlorodiphenylmethane (4-chlorohenzophenone dichloride) [Beil. V-592,  $\text{V}_1$ -(279)], h.p. 191–193° at 13 mm. (8), 189–194° at 12 mm. (25).  $D_4^{20} = 1.302$  (25),  $n_D^{20} = 1.6110$  (25); this prod. with  $\text{Zn}$  dust refluxed in dry ether for 1 hr. gives (12% yield (25))  $\alpha,\beta$ -di-(*p*-chlorophenyl)- $\alpha,\beta$ -di(phenyl)ethylenc, ndls. from alc., m.p. 202–203° (25).

$\bar{\text{C}}$  fused with  $\text{KOH}/\text{NaOH}$  gives (28) benzoic acid (66%) + *p*-chlorobenzoic acid (3:4940) (18%) + a little *p*-hydroxybenzoic acid (1:0340). —  $\bar{\text{C}}$  with 10% aq.  $\text{NaOH}$  in pres. of  $\text{Cu}$  under press. at 190° yields (29) 4-hydroxybenzophenone (1:1560).

[ $\bar{\text{C}}$  with  $\text{NH}_3$  in pres. of  $\text{Cu}$  cpds. at 170–300° under press. gives (30) 4-aminobenzophenone [Beil. XIV-81,  $\text{XIV}_1$ -(388)], lfts. from dil. alc., m.p. 123–124°. —  $\bar{\text{C}}$  condensed with  $\text{NaNH.C}_6\text{H}_5$  as directed (31) yields 4-anilinoenzophenoneanil, m.p. 56° (for other amines and use of products as antioxidants see (31)); note, however, that by a closely similar method (36) *p*-chlorobenzophenoneanil, m.p. 64–64.5°, can also be ohtd.]

$\bar{\text{C}}$  on dinitration with abs.  $\text{HNO}_3$  gives (32) a mixt. contg. 4-chloro-3,3'-dinitrobenzophenone, cryst. from toluene, m.p. 166°, 4-chloro-3,2'-dinitrobenzophenone, cryst. from alc., m.p. 123.5°, and 4-chloro-3,4'-dinitrobenzophenone, m.p. 136–136.5°.

⑥ 4-Chlorobenzophenone oxime: This prod. is known in two stereoisomeric forms: the higher-melting isomer, m.p. 155–156° (6) (corresp. acetate, m.p. 147–148° (6), corresp. benzyl ether, m.p. 74–75° (6)), which on Beckmann rearr. (6) (34) with  $\text{PCl}_5$ , with conc.  $\text{H}_2\text{SO}_4$  at 100°, or with  $\text{AcOH}/\text{Ac}_2\text{O}/\text{HCl}$  yields 4-chlorobenzanilide, is in the light of modern views on *trans* interchange regarded as the *syn*-(*p*-chlorophenyl) stereomer; the lower-melting isomer, m.p. 95° (6) (corresp. acetate, m.p. 105–106° (6), corresp. benzyl ether, m.p. 98–99° (6)), which on Beckmann rearr. with  $\text{PCl}_5$  yields benz-*p*-chloroanilide, is now regarded as the *trans*-(*p*-chlorophenyl) stereomer. (A mixt. of these two stereoisomeric oximes contg. 56% high-melting form + 44% low-melting form (33) is ohtd. from  $\bar{\text{C}}$  with  $\text{NH}_2\text{OH.HCl}$  + pyridine in abs. alc. (33) or from  $\bar{\text{C}}$  +  $\text{NH}_2\text{OH.HCl}$  + dil. alc.  $\text{KOH}$  (6); the two isomers are separated by means of their different solubilities in alc. (6) (34). — Note that the lower-melting isomer is itself converted to the higher-melting form by htg. 3 hrs. at 100° (6) and also (in part) during Beckmann rearr.]

⑦ 4-Chlorobenzophenone phenylhydrazone: cryst. from ether/ $\text{AcOH}$ , m.p. 106° (34). [From  $\bar{\text{C}}$  with phenylhydrazine or phenylhydrazine acetate in alc. as directed (34).]

— 4-Chlorobenzophenone *p*-nitrophenylhydrazone: unreported.

⑧ 4-Chlorobenzophenone 2,4-dinitrophenylhydrazone: m.p. 184–185° (Heilbron).

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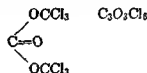
I 4559; *C.A.* 31, 705 (1937). (32) Montagne, *Ber.* 49, 2274-2276 (1916). (33) Bachmann,

Barton, *J. Org. Chem.* 3, 303-305 (1938). (34) Overton, *Ber.* 26, 27-28 (1893). (35) Adkins,

Cox, *J. Am. Chem. Soc.* 60, 1153 (1938). (36) Britton, Bryner (to Dow Chem. Co.), U.S. 1,938,

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3:1915 DI-(TRICHLOROMETHYL)  
CARBONATE  
(Triphosgene, perchlorodimethyl  
carbonate, hexachlorodimethyl  
carbonate)



Beil. III - 17

III<sub>1</sub>-(8)

III<sub>2</sub>-(16)

M.P. 78-79° (1)

79° (2) (3) (4)

B.P. 203° at 760 mm., sl. dec. (3)

124° at 50 mm. (3)

117° at 36 mm. (2)

105° at 22 mm. (2)

Cryst. from anhydrous ether (1) (2) or pet. eth. (4). — Disagreeable penetrating odor; attacks mucous membrane.

$\bar{\text{C}}$  on distn. dissociates slightly into phosgene (3:5000) and diphosgene (trichloromethyl chloroformate) (3:5515) (4) (5); solid  $\bar{\text{C}}$  when mixed with powdered charcoal and heated to just above m.p. rapidly decomposes to phosgene (3:5000) (5).

[For prepn. of  $\bar{\text{C}}$  from dimethyl carbonate (1:3016) by chlorination in sunlight see (1); from methyl chloroformate (3:5075) by chlorination see (2) ]

$\bar{\text{C}}$  on treatment at 20° for 1 hr. with NaI in acetone evolves CO and separates iodine to 84% of amt. expressed by the reactn.  $\text{Cl}_3\text{C.O.CO.O.CCl}_3 + 6\text{NaI} \rightarrow 3\text{CO} + 3\text{I}_2 + 6\text{NaCl}$  (6).

$\bar{\text{C}}$  with most reagents behaves like phosgene; e.g.,  $\bar{\text{C}}$  with alcohols gives ultimately dialkyl carbonates (7);  $\bar{\text{C}}$  with aniline in ether (7) or aq. (2) gives *N,N*-diphenylurea, m.p. 233° (7);  $\bar{\text{C}}$  with phenol + aq. NaOH gives (90% yield (7)) diphenyl carbonate (1:2335) cryst. from alc., m.p. 77.5-78° (7).

[For use of  $\bar{\text{C}}$  in prepn. of acid chlorides of carboxylic or sulfonic acids see (8); similarly  $\bar{\text{C}}$  htd. with anhydrous NaOAc yields  $\text{Ac}_2\text{O}$  (9) ]

3:1915 (1) Counselor, *Ber.* 13, 1697-1699 (1880). (2) Grignard, Rivat, Urbain, *Ann. chim.* (9) 13, 263-265 (1920). (3) Kling, Florentin, Jacob, *Ann. chim.* (9) 14, 208-210 (1920). (4)

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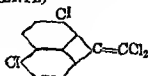
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now, Melnikov, *J. pr.* . . . . . (7) Nekras-

1934, II 2133. (9) . . . . . 4, 1933; *Cent.*

3334 (1932); *Cent.* 1932, II 2313. . . . . (31); *C.A.* 26,

3:1925 1,1-DICHLORO-2-(*o*-CHLOROPHENYL)-  
2-(*p*-CHLOROPHENYL)  
ETHYLENE



$C_{14}H_8Cl_4$  Beil. S.N. 480

M.P. 78.4-79.5° cor. (1)

Rectangular pl. from MeOH or EtOH.

[For prepn. of  $\bar{C}$  from 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane ("o,p'-DDT") (3:1820) by elimination of 1 HCl with alc. KOH on refluxing 3 hrs. (97% yield) see (1).]

$\bar{C}$  on oxidn. with  $CrO_3/AcOH$  gives (1) 2,4-dichlorobenzophenone (3:1565), m.p. 64.2-65.2° cor.

3:1925 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1599, 1602 (1945).

3:1930 1,2,5-TRICHLORONAPHTHALENE



$C_{10}H_5Cl_3$  Beil. V-544

V<sub>1</sub>—  
V<sub>2</sub>—

M.P. 79° (1)  
78-78.5° (2) (4)  
77° (3)  
(See text.)

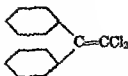
Cryst. volatile with steam. —  $\bar{C}$  if fused at 79° in cap. m.p. tube, and then allowed to cool slowly in the bath or rapidly in air, solidifies at 69° to a translucent cryst. mass which (if the temperature is immediately raised) melts at 74° but if allowed to remain at or below 69° for a few minutes becomes opaque and then melts at 79° (1).

[For prepn. of  $\bar{C}$  from 1-chloro-5-sulfonaphthylamine-2 [Beil. XIV-750] via diazotization and use of  $Cu_2Cl_2$  reactn. see (1) (4); from 1-chloro-2-nitronaphthalenesulfonic acid-5 [Beil. XI-170] (3), 2-chloro-1-nitronaphthalenesulfonyl chloride-5 [Beil. XI-169] (3), 2-chloronaphthalene-1,5-bis-(sulfonyl chloride) [Beil. XI-213] (5), or 1,2-dichloronaphthalene-sulfonic acid-5 [Beil. XI-163] (2) with  $PCl_5$  see iodic. refs.)

( $\bar{C}$  treated with  $ClSO_3H$  in  $CS_2$  and conv. to K salt as directed (1) gives a mixt. contg. 70% (less sol.) K 1,2,5-trichloronaphthalenesulfonate-X (corresp. sulfonyl chloride, m.p. 146°) and 30% (more sol.) K 1,2,5-trichloronaphthalenesulfonate-Y (corresp. sulfonyl chloride, m.p. 179°).]

3:1930 (1) Turner, Wynne, *J. Chem. Soc.* **1941**, 247, 251-252. (2) Armstrong, Wynne, *Chem. News* **59**, 188 (1889). (3) Cleve, *Chem. Ztg.* **17**, 398 (1893). (4) Armstrong, Wynne, *Proc. Chem. Soc.* **1889**, 36, 49. (5) Armstrong, Wynne, *Chem. News* **62**, 164 (1890).

## 3:1938 1,1-DICHLORO-2,2-DIPHENYLETHYLENE

 $C_{14}H_{10}Cl_2$ 

Beil. V - 639

V<sub>1</sub>—V<sub>2</sub>-(545)

M.P. 80°	(1) (2)	B.P. 336° cor.	(5) (6)
	(5) (6) (13)	316.5° cor.	(7)
78.0-79.5°	(3)	315° u.c.	(5) (6)
78.5°	(4)		

Colorless cryst. from alc.; 100 pts. 90% alc. dis. in cold 11.91 pts.  $\bar{C}$ , on boilg. 19.87 pts.  $\bar{C}$  (8). —  $\bar{C}$  is eas. sol. ether,  $CHCl_3$ , or  $CS_2$ ; less so in alc. or  $C_6H_6$ .

PREPARATION OF  $\bar{C}$ 

[For prepn. of  $\bar{C}$  from 1,1,1-trichloro-2,2-diphenylethane (3:1420) by splitting out 1 HCl on distn. (9) cf. (19) (6), or with alc. KOH (2) (1) (for study of rate see (11)), or alc. NaOEt (1) see indic. refs.; from *unsym.*-diphenylethane [Beil. V-605, V<sub>1</sub>-(285), V<sub>2</sub>-(509)] with  $Cl_2$  at 100-150° in quartz flask in light for 10 hrs followed by distn. at ord. press. (16% yield) see (3); from *unsym.*-diphenylethylene [Beil. V-639, V<sub>1</sub>-(368), V<sub>2</sub>-(543)] with  $Cl_2$  followed by distn. see (12).]

[For formn. of  $\bar{C}$  from  $\alpha,\alpha$ -dichloro- $\beta,\beta$ -diphenylethylene sulfide ( $Cl_2C-CH(C_6H_5)_2$ ) by



htg. at 100° for 2 hrs. (or for shorter time at 160°), or by boilg. with MeOH, or htg. with Zn see (13); from  $\alpha,\alpha$ -dichloro- $\beta,\beta$ -diphenylethyl *p*-tolyl sulfone with  $PCl_5$  at 200° for 2 hrs. see (4); for formn. of  $\bar{C}$  during condensation of chloral (3:5210) with  $C_6H_6 + AlCl_3$  in  $CS_2$  see (10) (6).]

CHEMICAL BEHAVIOR OF  $\bar{C}$ 

Reduction. [ $\bar{C}$  on reduction with conc. HI + P at 170-210° gives (7) *unsym.*-diphenylethane [Beil. V-605, V<sub>1</sub>-(285), V<sub>2</sub>-(509)] and bibenzyl (1:7149).]

Addition of halogens.  $\bar{C}$  with  $Cl_2$  in dry  $CHCl_3$  adds 1 mole halogen giving (8) (5) 1,1,1,2-tetrachloro-2,2-diphenylethane, m.p. 35° (6). —  $\bar{C}$  with excess  $Br_2$  htd. on aq. bath until excess reagt. evaporates gives (6) 1,2-dibromo-1,1-dichloro-2,2-diphenylethane, cryst. from alc., m.p. 120.0-120.5° (6).

Behavior with alkalis. [ $\bar{C}$  with aq. NaOH at 150°, or with alc. NaOH in s.t. at 100°, is substantially unaffected within 24 hrs. (3); however,  $\bar{C}$  with alc. KOH in stainless-steel bomb at 150° for 24 hrs. gives (73% yield (3)) diphenylacetic acid (1:0765), m.p. 147-148° cor. (3) cf. (1). — Note also that, although  $\bar{C}$  with dry NaOMe in  $C_6H_6$  does not react even in s.t. at 180° for 36 hrs. yet  $\bar{C}$  with dry NaOMe (2 moles) on direct distn. gives diphenylacetylene (tolane) and other products (15).]

[Note also that  $\bar{C}$  with Na phenolate at 225° for 24 hrs. gives (3)  $\alpha$ -hydroxy- $\alpha,\alpha$ -diphenylacetaldehyde diphenylacetal (benzaldehyde diphenylacetal), m.p. 111.5°-112° (3).]

Behavior with  $H_2SO_4$  or  $HNO_3$ . With  $H_2SO_4$ .  $\bar{C}$  with conc.  $H_2SO_4$  on warming first becomes yellow, then dark green, later violet, and ultimately brownish red. (5) (6).

With  $HNO_3$ .  $\bar{C}$  on addition to 12 pts. ice-cold fuming  $HNO_3$  and subsequently pouring onto ice gives (14) 1,1-dichloro-2,2-bis-(*p*-nitrophenyl)ethylene, yellowish ndis. from hot alc., m.p. 172° (14); note also that from the mother liquors of recrystn. there can also be obtd. some 4,4'-dinitrobenzophenone, m.p. 153-159°, resulting from some simultaneous oxidn. (14).



Colorless shining lfts. (from alc.) with camphoraceous odor. Eas. sol. ether,  $C_6H_6$ ,  $CHCl_3$ , or  $CCl_4$ .

[For prepn. of  $\bar{C}$  (100% yield (1)) from the solid stereoisomer (3:0870) of 1,2,3,4-tetrachlorobutadiene-1,3 see (1); for formn. of  $\bar{C}$  from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) by actn. of u.v. light see (1).] [Note that octachlorobutane (3:2000) has also been reported in same reactn.] [For formn. of  $\bar{C}$  together with its liquid stereoisomer (3:9046) by actn. of  $Cl_2$  upon the high-boilg. fraction obtd in the prepn. of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1).]

$\bar{C}$  in alc. refluxed with Zn/Cu couple for 1 hr. yields (1) the solid stereoisomer of 1,2,3,4-tetrachlorobutadiene-1,3 (3:0870), m.p.  $50^\circ$  (1).

3:1945 (1) Müller, Hüther, *Ber.* 64, 559-600 (1931); *C.A.* 25, 3956-3957 (1931).

### 3:1960 PIPERONYLOYL CHLORIDE

(3,4-Methylenedioxy-  
benzoyl chloride)



$C_8H_6O_3Cl$

Beil. XIX - 270

XIX<sub>1</sub>—

M.P.  $80^\circ$  (1) (2)

B.P.  $155^\circ$  at 25 mm. (2)  
 $140-141^\circ$  at 8 mm. (1)

[For prepn. of  $\bar{C}$  from piperonylic acid (1:0865) with excess  $SOCl_2$  at  $100^\circ$  (1) or in  $C_6H_6$  (90-95% yield (4)), or with  $PCl_5$  (2), see indic. refs. — Note, however, that at higher temps. the dioxymethylene group is also attacked: e.g., piperonylic acid htd. in a s.t. with  $SOCl_2$  at  $180-200^\circ$  for 8 hrs. (1) or refluxed 3 hrs. with 3 moles  $PCl_5$  (1) yields  $\mu,\mu$ -dichloropiperonyl chloride (Beil. XIX-272, XIX<sub>1</sub>-(743)), b.p.  $140-150^\circ$  at 12 mm. (1).]

$\bar{C}$  with diazomethane yields (3) piperonyl diazomethyl ketone which with ammonia yields (3) homopiperonylamide, m.p.  $173^\circ$ ;  $\bar{C}$  with ethyl sodio-acetoacetate in dry ether, followed by hydrolysis (as specified (4)) of the acetyl group, yields ethyl piperonylacetate, m.p.  $42.5^\circ$  (4).]

$\bar{C}$  on hydrolysis with aq. yields piperonylic acid (1:0865), m.p.  $228^\circ$ .

① Piperonylamide [Beil. XIX-270]: this. from alc., m.p.  $169^\circ$ .

② Piperonylanilide [*N*-phenyl-piperonylamide]: cryst. from dil. alc., m.p.  $146-147^\circ$  cor. (5). [From  $\bar{C}$  + 2 moles aniline in  $C_6H_6$  (5).]

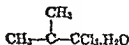
③ Piperonylo-*p*-toluidide: cryst. from dil. alc., m.p.  $149-149.5^\circ$  cor. (5). [Similarly using *p*-toluidine (5).]

④ Piperonylo- $\alpha$ -naphthalide: cryst. from dil. alc., m.p.  $192-193^\circ$  cor. (5). [Similarly using  $\alpha$ -naphthylamine (5).]

⑤ Piperonylo- $\beta$ -naphthalide: cryst. from dil. alc., m.p.  $156.5-157^\circ$  cor. (5). [Similarly using  $\beta$ -naphthylamine (5).]

3:1960 (1) Barger, *J. Chem. Soc.* 93, 567-568 (1908). (2) Perkin, Robinson, *Chem. News* 92, 293 (1905). (3) Arndt, Eistert, *Ger.* 650,706, Sept. 30, 1937; *Cent.* 1937, II 4390, *C.A.* 32, 595 (1938). (4) Bruchhausen, Gerhard, *Ber.* 72, 835-836 (1939). (5) Gertler, Haller, *J. Am. Chem. Soc.* 64, 1741 (1942).

### 1,1,1-TRICHLORO-2-METHYL- PROPANOL-2 HYDRATE



M.P.  $80-81^\circ$

See 3:2662 under anhydrous product.



## 3:1975 1,3,6-TRICHLORO-NAPHTHALENE

 $C_{10}H_5Cl_3$ 

Beil. V - 646

V<sub>1</sub>—V<sub>2</sub>—

M.P. 80.5°-81° (1) (2)

[For prepn. of  $\bar{C}$  from 3,6-dichloronaphthalenesulfonyl chloride-1 (1), from 6-chloronaphthalene-1,3-bis-(sulfonyl chloride) [Beil. XI-212] (2), from 3-chloronaphthalene-1,6-bis-(sulfonyl chloride) [Beil. XI-214] (2), from 1-chloronaphthalene-3,6-bis-(sulfonyl chloride) [Beil. XI-217] (3), or from 1-nitronaphthalene-3,6-bis-(sulfonyl chloride) [Beil. XI-218] (1) (3) (4), each with  $PCl_5$  as directed, see indic. refs.]

[ $\bar{C}$  treated with  $ClSO_3H$  in  $CS_2$  and prod. converted to sodium salt yields (1) sodium 1,3,6-trichloronaphthalenesulfonate-7 (corresp. sulfonyl chloride, m.p. 156° (1)).]

3:1975 (1) Turner, Wynne, *J. Chem. Soc.* 1941, 247, 253, 256. (2) Armstrong, Wynne, *Chem. News* 62, 164-165 (1890). (3) Armstrong, Wynne, *Chem. News* 71, 254 (1895). (4) Armstrong, Wynne, *Proc. Chem. Soc.* 1895, 81.

## 3:1900 1,3-DICHLORONAPHTHOL-2

 $C_{10}H_6OCl_2$ 

Beil. VI - 649

VI<sub>1</sub>—VI<sub>2</sub>-(604)

M.P. 80-81° (1)

78° (2)

Ndls. from lgr.; eas. sol. alc., ether, AcOH, or  $C_6H_6$  (1).

[For prepn. see Beil. VI-649 and (2).]

$\bar{C}$  in AcOH oxidized with conc.  $HNO_3$  ( $D = 1.42$ ) yields mainly 3-chloronaphthoquinone-1,2 [Beil. VII-720], red ndls. from  $CHCl_3$ , m.p. 172° (1).

$\bar{C}$  in alc. boiled 15 hrs. with coppered Zn dust yields 3-chloronaphthol-2 (3:2545), m.p. 93° (4); but  $\bar{C}$  is not reduced by Na/Hg (3).

[For study of reaction of  $\bar{C}$  with alkali sulfites see (5).]

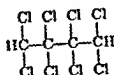
① 1,3-Dichloro-2-naphthyl acetate: from  $\bar{C}$  + AcCl; m.p. 79-80° (1). [Note that this m.p. is close to that of original  $\bar{C}$ .]

3:1990 (1) Zincke, *Ber.* 21, 3385-3387 (1888). (2) Fries, Schimmelschmidt, *Ann.* 484, 297 (1930). (3) Marschalk, *Bull. soc. chim.* (4) 43, 1361 (1928). (4) Herzberg, Spengler, Schmid (to I.G.), Ger. 431,165, June 30, 1926; *Cent.* 1926, 1196 (1926). (5) Marschalk, *Bull. soc. chim.* (4) 45, 651-662 (1929).

CHAPTER VI  
DIVISION A. SOLIDS

(3:2000-3:2109)

3:2000 1,1,2,2,3,3,4,4-OCTA-  
CHLOROBUTANE


$$\text{C}_4\text{H}_2\text{Cl}_8$$

Bell. S.N. 10

M.P. 81° (1)

Colorless cryst. (from alc. with odor resembling honey-

Colorless cryst. (from alc. with odor resembling honey).  
[For formn. of **5** from 1,1,2,2-tetrachloroethane (neethylene tetrachloride) (3:5750) by protracted action of ultra-violet light see (1), considerable amts. of dichloroacetic acid (3:6208), m p. 10.85°, and small amts. of oxalic acid (1:0445) are also formed (1), and the solid stereoisomer (3:1915) of 1,1,2,3,4,4-hexachlorobutene-2, m p. 81° has also been reported (3) from the same reaction.]  
[**5** (3:5750) obtd. (2) from trichloroethylene (3:5170) by

[An octachlorobutane of m.p. 75.0–76.0° obtd. (2) from trichloroethylene (3:5170) by actn. of  $F_2$  is not regarded (2) as having the structure of C]

3:2000 (1) Möller, Luber, *Ber.* 65, 955-957 (1932). (2) Möller, *J. Am. Chem. Soc.* 62, 343 (1940).  
(3) Möller, Huther, *Ber.* 64, 599 (1931).

3:2100 2,4,5-TRICHLOROTOLUENE

 $C_7H_5Cl_3$ 

BeLL V - 290  
V<sub>1</sub>-(152)  
V<sub>2</sub>-(232)

M.P. 82.4° (1)  
82° (2) (3) (4)  
(5)  
81-82° (6) (13)  
80-81° (6)

B.P. 229-230° at 716 mm. (2)  
230° at 715 mm. (4)

White nids. or lfts. from nlc. [For sepn. of C from 2,3,4-trichlorotoluene (3:0125) by sulfonation of latter under conditions not affecting C see (2) (7) ]

[For prepn. of **5** from 4,5-dichloro-2-aminotoluene (Beil. XII-837) (8), or from 4,5-dichloro-3-aminotoluene (Beil. XII-872) (8) (5), or from 2,5-dichloro-4-aminotoluene (Beil. XII-900) (3), via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reactn. see indic. refs., from toluene +  $\text{AlCl}_3$  with  $\text{SO}_2\text{Cl}_2$  at  $70^\circ$  (40% **5** + 31% 2,3,4-trichlorotoluene (3-0425) (11) see (1))

(10) or  $\text{MoCl}_5$  (11) or  $\text{FeCl}_3$  (11) on silica gel (4), or by electrolysis in  $\text{HCl}/\text{AcOH}$  soln. (12), see inde. refs.; from *o*-chlorotoluene (3:8215) or *p*-chlorotoluene (3:8257) with  $\text{Cl}_2$  in pres. of  $\text{MoCl}_5$  or  $\text{FeCl}_3$  see (2); from 2,4-dichlorotoluene (3:6790) in pres. of  $\text{Al}/\text{Hg}$

(13) or Fe (6) or from 3,4-dichlorotoluene (3:6355) in pres. of Al/Hg (13) see indic. refs.; from sodium *p*-toluenesulfonate with Cl<sub>2</sub> see (14).]

[C̄ with Cl<sub>2</sub> yields (15) 2,4,5-trichlorobenzal dichloride (3:6910) (together with other products).]

C̄ on mononitration, e.g., by soln. in HNO<sub>3</sub> (*D* = 1.52) yields (16) (2) (8) 2,4,5-trichloro-3-nitrotoluene [Beil. V-333], ndls. from alc., m.p. 92° (2), 91-92° (8), 88.5-90.5° (17), 88.5° (16) (note that the isomeric 2,4,5-trichloro-6-nitrotoluene (prepd. indirectly (18)) has m.p. 93-94° (18)); C̄ on dinitration, e.g., on warming with a mixt. of HNO<sub>3</sub> (*D* = 1.5) + conc. H<sub>2</sub>SO<sub>4</sub>, yields (16) (2) (8) 2,4,5-trichloro-3,6-dinitrotoluene [Beil. V-346], ndls. from alc., m.p. 227° (1) (2), 226-227° (8), 226° u.c. (18), 225° (16).

C̄ on oxidn. with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>SO<sub>4</sub> (19) or with dil. HNO<sub>3</sub> in s.t. at 150° (8) (6) yields 2,4,5-trichlorobenzoic acid (3:4630) q.v.

3:2100 (1) Silberrad, *J. Chem. Soc.* 127, 2681 (1925). (2) Seelig, *Ann.* 237, 131, 140, 156 (1887). (3) Morgan, Drew, *J. Chem. Soc.* 117, 789 (1920). (4) Firth, Smith, *J. Chem. Soc.* 1936, 339. (5) Musante, Fusco, *Gazz. chim. ital.* 66, 645 (1936). (6) Feldman, Kopeliowitsch, *Arch. Pharm.* 273, 493-495 (1935). (7) Prentzell, *Ann.* 296, 181-182 (1897). (8) Cohen, Dakin, *J. Chem. Soc.* 81, 1332-1335 (1902). (9) Limpricht, *Ann.* 139, 326 (1866). (10) Beilstein, Kuhlberg, *Ann.* 146, 326 (1868).

(11) Aronheim, Dietrich, *Ber.* 8, 1405 (1875). (12) Fichter, Glantzstein, *Ber.* 49, 2481-2487 (1916). (13) Ref. 8, pp. 1340-1343. (14) British Dyestuffs Lds., Green, Chibben, *Brit.* 169,025, Oct. 13, 1921, *Cent.* 1922, IV 376. (15) Leopold Cassella Co., *Ger.* 363,290, Nov. 6, 1922; *Cent.* 1923, II 482-483. (16) Schultz, *Ann.* 187, 277, 280 (1877). (17) Qvist, Holmberg, *Acta Acad. Aboensis Math. et Phys.* 6, No. 14, 3-28 (1932); *Cent.* 1932, II 2815-2816; *C.A.* 27, 5726-5727 (1933). (18) Levy, Stephen, *J. Chem. Soc.* 1931, 78. (19) Jannasch, *Ann.* 142, 301 (1867).

**3:2115 5-CHLORO-2,3-DIMETHYL-  
PHENOL**  
(5-Chloro-*o*-3-xyleneol)



C<sub>8</sub>H<sub>7</sub>OCl

Beil. VI —  
VI<sub>1</sub>—  
VI<sub>1</sub>-(454)

M.P. 82° (1)  
81-82° (2)

Ndls. from hot lt. pet. in which it is readily sol. hot hut spar. sol. cold. — Volatile with steam.

[For prepn. of C̄ from 5-amino-2,3-dimethylphenol (5-amino *o*-3-xyleneol) [Beil. XII1- (244)] (3) via diazotization and use of Cu<sub>2</sub>Cl<sub>2</sub> reaction (yield not stated) see (2); for formn. of C̄ from 4,5-dichloro-1,1-dimethylcyclohexen-5-one-3 on hgt. see (1).]

C̄ with Cl<sub>2</sub> in lt. pet. gives (2) 4,5,6-trichloro-2,3-dimethylphenol (3:4742), m.p. 180-181°.

The nitration of C̄ has not been reported, and none of the products to be expected is known.

— 5-Chloro-2,3-dimethylphenyl acetate: unreported.

Ⓓ 5-Chloro-2,3-dimethylphenyl benzoate: pr. from alc., m.p. 88° (2).

3:2115 (1) Hinkel, *J. Chem. Soc.* 125, 1852 (1924). (2) Hinkel, Collins, Ayling, *J. Chem. Soc.* 123, 2970-2971 (1923). (3) Crossley, *J. Chem. Soc.* 103, 2181 (1913).

## 3:2125 1,2,3-TRICHLORONAPHTHALENE

 $C_{10}H_7Cl_3$ 

Beil. V - 544

V<sub>1</sub>—V<sub>2</sub>—

M.P. 82-83° (1)

81° (2)

80.5° (1)

(See text.)

Pr. from ether + alc. — The behavior of  $\bar{C}$  on fusion is characteristic: if the fused  $\bar{C}$  in a m.p. tube is allowed to cool to 68° and then withdrawn, it immediately solidifies to a translucent mass which on swift reimmersion into the bath shows m.p. 66-67° but if left for a few seconds in the air suddenly becomes opaque forming a cylinder of m.p. 82-83°, retracted from the wall of the capillary m.p. tube. This change (although slower) also occurs in the translucent form if cooled below 66° (1).

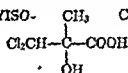
[For prepn. of  $\bar{C}$  from 1-chloronaphthalene tetrachloride [Beil. V-493] with alc. NaOEt (61.6% yield (1)) (2) (3) see indic. refs.; from 1,3-dichloronaphthol-2 (3:1990) by distn. with  $PCl_5$  see (2); from sodium 1,2,3-trichloronaphthalenesulfonate-7 (1) by hydrolysis with superhdt. steam see (1).]

[ $\bar{C}$  treated with  $ClSO_3H$  in  $CS_2$  and reacta. prod. conv. to sodium salt as directed (1) gives mixt. of sodium 1,2,3-trichloronaphthalenesulfonate-5 (corresp. sulfonyl chloride, m.p. 131°, corresp. sulfonamide, m.p. 249°) and sodium 1,2,3-trichloronaphthalenesulfonate-7 (corresp. sulfonyl chloride, m.p. 157°, corresp. sulfonamide, m.p. 245°) (1).]

[ $\bar{C}$  with 7 pts. fuming  $H_2SO_4$  (10%  $SO_3$ ) shaken 15 min. at 100° yields (1) 1,2,3-trichloronaphthalene-5,7-disulfonic acid (corresp. bis-(sulfonyl chloride), m.p. 184° (1)).]

3:2125 (1) Turner, Wynne, *J. Chem. Soc.* 1941, 248-251. (2) Faust, *Saame*, *Ann.* 160, 71 (1871).

(3) Armstrong, Wynne, *Chem. News* 61, 285 (1890).

3:2145  $\beta,\beta$ -DICHLORO- $\alpha$ -HYDROXYISOBUTYRIC ACID $C_4H_5O_3Cl_2$ 

Beil. III - 317

III<sub>1</sub>—III<sub>2</sub>-(224)

M.P. 82-83° (1) (2)

Neut. Eq. 173

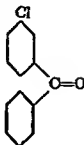
Pr. from EtOH/ether (1). — Cannot be distd. without decompn. but sublimes.

[For prepn. from  $\beta,\beta$ -dichloro- $\alpha$ -hydroxyisobutyronitrile (addn. prod. from  $\alpha,\alpha$ -dichloroacetone (3:5430) +  $HCN$ ) [Beil. I-317] by digestion with strong  $HCl$  at 100° see (1).]

The corresp. anilide has been prepd. indirectly by interaction of phenyl isocyanide with  $\alpha,\alpha$ -dichloroacetone (3:5430) in aq. (2); pr. from  $CHCl_3$ , m.p. 132-133° (2).

3:2145 (1) Bischoff, *Ber.* 8, 1334 (1875). (2) Passerini, *Gazz. chim. ital.* 54, 540 (1924).

**3:2160 3-CHLOROBENZOPHENONE**  
(*m*-Chlorophenyl phenyl  
ketone)

 $C_{13}H_9OCl$ Beil. VII - 419  
VII<sub>1</sub>-(227)

M.P. 82-83° (1) (6)

82° (2) (3)

81° (4) (5)

Microscopic ndls. from alc. (1) (6) or *n*-PrOH (2); spar. sol. alc. (1), pet. ether (6), eas. sol.  $C_6H_6$  (6).

[For prepn. from *m*-chlorobenzoyl chloride (3:6590) +  $C_6H_6$  +  $AlCl_3$  (64.7% yield (2)) see (2) (1) (6) (5).]

$\bar{C}$  on reduction with Na/Hg + alc. (100% yield (7)) or Al/Hg + 80% alc. (4) or boilg. alc. KOH (8) yields exclusively 3-chlorodiphenylcarbinol [Beil. VI<sub>1</sub>-(327)], m.p. 40° (7), 39-40° (5), 38° (4). —  $\bar{C}$  with Zn + AcOH (7) or  $\bar{C}$  in alc. on long exposure to sunlight (7) gives *sym*,-3,3'-dichlorohenzpinacol [Beil. VI<sub>1</sub>-(523)], cryst. from pet. eth., m.p. 137-138° (7), 135° (4).

$\bar{C}$  fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (3) BzOH (1:0715) (80% yield (3)) and a little (5%) (3) *m*-chlorobenzoic acid (3:4302), m.p. 158° (3), together with chlorobenzene (3:7903) from cleavage of most of the *m*-chlorobenzoic acid

$\bar{C}$  with  $CH_3MgI$  yields (2) 1-(*m*-chlorophenyl)-1-phenylethylene, oil, h.p. 152-153° at 14 mm. (2).

③ 3-Chlorobenzophenone oxime: from  $\bar{C}$  +  $NH_2OH \cdot HCl$  + alk.; the two stereoisomers are sepd. by fractnl. pptn. of their AcOH soln. with aq. (1).

$\alpha$ -form (less-sol. isomer); cryst. pdr., m.p. 132-133° (1). [With  $PCl_5$  in dry ether, followed by aq., this form yields *m*-chlorobenzanilide [Beil. XII-267], cryst. from alc., m.p. 122-125° (1).]

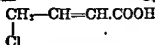
$\beta$ -form (more-sol. isomer); cryst. pdr., m.p. 105-106° (1). [With  $PCl_5$  in dry ether, followed by aq., this forms *henz-m*-chloroanilide [Beil. XII-605], ndls. from alc., m.p. 118° (1), accompanied by some *m*-chlorobenzanilide (see above) (1).]

3:2160 (1) Hantzsch, *Ber.* 24, 57-58 (1891). (2) Bergmann, Bondi, *Ber.* 64, 1477 (1931). (3) Lock, Rödiger, *Ber.* 72, 867 (1939). (4) Cohen, Böeseken, *Rec. trav. chim.* 38, 115, 123 (1919). (5) Norris, Blake, *J. Am. Chem. Soc.* 50, 1812 (1928). (6) Koopal, *Rec. trav. chim.* 34, 153 (1915). (7) Ref. 6, pp. 160-161. (8) Montagne, van Charante, *Rec. trav. chim.* 31, 312 (1912)

**3:2170  $\gamma$ -CHLOROCROTONIC ACID**

(4-Chlorohuten-2-oic  
acid-1) $C_4H_5O_2Cl$ 

Beil. II-418



M.P. 83° (1)

82° (2)

81-82° (3) (4)

B.P. 117-118° at 13 mm. (5)

White cryst., eas. sol. ether or AcOH, can be recrystallized from pet. ether (1) or from hot aq. (5). —  $\bar{C}$  distills under reduced press. without decomposition (5). — Note that m.p. 76.7-77.5° first reported (5) was later (2) found to be erroneous and same sample had actually m.p. 81-82° (2).

Note that, although  $\bar{C}$  is capable of existing in two geometrically isomeric forms, only this one is known; collateral evidence (but not actual proof) indicates that  $\bar{C}$  probably represents the *trans* stereoisomer.

[For prepn. of  $\bar{C}$  from ethyl  $\gamma$ -chlorocrotonate (3:8657) by hydrolysis with  $\text{Ba}(\text{OH})_2$  below  $0^\circ$  (60% yield (1) (6)) (4), or less advantageously with 30% aq. KOH in alc. soln. at  $-15^\circ$  (40% yield (1)) (5) (note that  $\gamma$ -chlorovinylacetic acid, m.p.  $10^\circ$  (1), is often obtd. (1) (4) as by-prod.); for formn. of  $\bar{C}$  from  $\beta$ - $\gamma$ -dichloro-*n*-butyric acid [Beil. II-280] with KOH (poor yield (5)), from *trans*- $\gamma$ -hydroxycrotonic acid [Beil. III-376] with  $\text{SOCl}_2$  in pyridine (2), or from methyl  $\alpha$ -chloro- $\alpha$ -vinylacetate by hydrolysis (3) (7) (presumably as a result of allylic transposition of  $\alpha$ -chloro- $\alpha$ -vinylacetic acid under the influence of alkali) see indic. refs.]

$\bar{C}$  dissolved in excess aq. 1 *N* NaOH and shaken with  $\text{H}_2$  in pres. of Pd/activated carbon is readily dehalogenated giving (95% yield (1)) crotonic acid (1:0425); with sufficient  $\text{H}_2$  this prod. ultimately reduces to *n*-butyric acid (1:1035).

[ $\bar{C}$  by cat. hydroxylation with  $\text{BaClO}_3$ /osmic acid gives (yields: 75% (6), 78% (9)) *threo*- $\gamma$ -chloro- $\alpha,\beta$ -dihydroxy-*n*-butyric acid, m.p.  $100^\circ$  (9); this prod. with silver oxide as directed replaces Cl by OH giving (59% yield (6)) *d,l*-threonic acid, m.p.  $98^\circ$  (6).]

$\bar{C}$  adds  $\text{Br}_2$  (1 mole) yielding (3)  $\gamma$ -chloro- $\alpha,\beta$ -dibromo-*n*-butyric acid, cryst. from cyclohexane, m.p.  $119$ - $120^\circ$  (3)

$\bar{C}$  with NaI in dry acetone ppts. NaCl and gives (86% yield (1))  $\gamma$ -iodocrotonic acid, yel. ndls. from lgr., m.p.  $108$ - $108.5^\circ$  (1).

[ $\bar{C}$  on neutralization with  $\text{NH}_4\text{OH}$  and htg. with  $(\text{NH}_4)_2\text{SO}_3$  at  $50^\circ$  for 12 hrs. gives (4)  $\gamma$ -sulfocrotonic acid, very hygroscopic cryst., m.p.  $94$ - $96^\circ$ .]

The acid chloride corresponding to  $\bar{C}$  is unreported.

— Methyl  $\gamma$ -chlorocrotonate: unreported.

— Ethyl  $\gamma$ -chlorocrotonate: b.p.  $191$ - $193^\circ$  at 760 mm. (5) (see 3:8657).

—  $\gamma$ -Chlorocrotonamide: cryst. from hot aq., m.p.  $135.5$ - $136^\circ$  (8),  $130$ - $132^\circ$  (5).

[Reported only by partial hydrolysis of  $\gamma$ -chlorocrotononitrile (5) (8).]

—  $\gamma$ -Chlorocrotonanilide: unreported.

3:2170 (1) Braun, *J. Am. Chem. Soc.* 52, 3167-3176 (1930). (2) Rambaud, *Bull. soc. chim.* (5) 1, 1340 (1934). (3) Rambaud, *Bull. soc. chim.* (5) 1, 1348 (1934) (4) Backer, Benninga, *Rec. trav. chim.* 55, 610 (1936). (5) Lespieau, *Bull. soc. chim.* (3) 33, 466-467 (1905). (6) Glattfeld, Rietz, *J. Am. Chem. Soc.* 62, 976 (1940). (7) Rambaud, *Compt. rend.* 197, 769 (1933). (8) Berthet, *Bull. acad. roy. Belg., Classe sci.* 27, 212-228 (1941); *Cent.* 1912, I 2115-2116; *C.A.* 37, 3400 (1943). (9) Braun, *J. Am. Chem. Soc.* 52, 3176-3185 (1930).

### 3:2174 2,4,6-TRICHLORORESORCINOL



$\text{C}_6\text{H}_3\text{O}_2\text{Cl}_3$

Beil. VI-820

VI—

VI—

M.P.  $83^\circ$  (1) (2) (3) (4)

Colorless cryst. from hot aq. (2). —  $\bar{C}$  is spar. sol. cold aq.; eas. sol. alc., ether.  $\bar{C}$  sublimes but with appreciable decompn.

[For prepn. of  $\bar{C}$  from resorcinol (1,3-dihydroxybenzene) (1:1530) with  $\text{Cl}_2$  in aq. (4),  $\text{AcOH}$  (3) (2), or  $\text{CHCl}_3$  (2), or with  $\text{SO}_2\text{Cl}_2$  (excess) (4) or with dichlorourea (1), see indic. refs.]

[For formn. of  $\bar{C}$  from 2,4,4,6,6-pentachlorocyclohexen-1-dione-3,5 ("pentachlororesorcinol") [Beil. VII-572, VII-323]] by reduction with sulfite (2) (5) or  $\text{SnCl}_2$  (2) see

indic. refs.; from 2,2,4,4,5,6,6-heptachlorocyclohexanedione-1,3 ("heptachlorodihydroresorcinol") [Beil. VII-555] by similar reduction see (6).]

[ $\bar{C}$  on oxidn. with alk.  $K_3Fe(CN)_6$  gives (7) a yel. prod., m.p. 60°.]

$\bar{C}$  in not too dilute aq. soln. with  $FeCl_3$  gives on warming a wine-red color (4).

— 2,4,6-Trichlororesorcinol dimethyl ether: unreported. [A prod. of m.p. 174° which may have this structure has been reported by indirect means (8).]

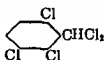
— 2,4,6-Trichlororesorcinol diethyl ether: unreported.

⑦ 2,4,6-Trichlororesorcinol diacetate: cryst. from alc., m.p. 116° (2).

⑧ 2,4,6-Trichlororesorcinol dibenzoate: pr. from alc., m.p. 133° (4). [From  $\bar{C}$  with  $BzCl$  on htg. (4).]

3:2174 (1) Likhoshershtov, *J. Gen. Chem. (U.S.S.R.)* 3, 164-171 (1933); *Cent.* 1934, I 1876; *C.A.* 28, 1075 (1934). (2) Zinke, Rabinowitsch, *Ber.* 23, 3776-3777 (1890). (3) Benedikt, *Monatsh.* 4, 224-226 (1883). (4) Reinhard, *J. prakt. Chem.* (2) 17, 336-341 (1878). (5) Claassen, *Ber.* 11, 1441 (1878). (6) Zinke, Rabinowitsch, *Ber.* 24, 913 (1891). (7) Stenhouse, Groves, *Ber.* 13, 1307 (1880). (8) Ciamician, Silber, *Ber.* 24, 2979-2980 (1891).

3:2178 2,3,6-TRICHLOROBENZAL (DI)-  
CHLORIDE  
(2,3,6-Trichlorobenzylidene (di)-  
chloride)



$C_7H_3Cl_4$  Beil. S.N. 466

M.P. 83° (1) B.P. 145-150° at 12 mm. (1)

Colorless ndls. from MeOH.

[For prepn. of  $\bar{C}$  (81% yield) from 2,3,6-trichlorobenzaldehyde (3:2287) with  $PCl_5$  see (1).]

Note that  $\bar{C}$  depresses the m.p. (86-87°) of the corresp. aldehyde (3:2287).

[For study of rate of hydrolysis of  $\bar{C}$  see (1).]

3:2178 (1) Asinger, Lock, *Monatsh.* 62, 338 (1933).

3:2180 4-CHLORO-2,6-DIMETHYL-  
PHENOL  
(5-Chloro-*m*-2-xenol)



$C_8H_9OCl$  Beil. S.N. 529

M.P. 83° (1)

[For prepn. of  $\bar{C}$  from 4-chloro-2,6-dimethylphenol (*vic-m*-xenol) (1:1425) by chlorination with  $SO_2Cl_2$  in AcOH (100% yield) see (1).]

[For study of bactericidal action of  $\bar{C}$  see (1).]

— 4-Chloro-2,6-dimethylphenyl acetate: unreported.

— 4-Chloro-2,6-dimethylphenyl benzoate: unreported.

3:2180 (1) Heicken, *Angew. Chem.* 52, 264-265 (1939).

3:2182 2,4-DICHLORO-3,5-DIMETHYL-  
PHENOL  
(2,4-Dichloro-*m*-5-xenol)



$C_8H_7OCl_2$  Beil. VI—  
VI<sub>1</sub>—  
VI<sub>2</sub>-(464)

M.P. 83° (1)

Cryst. from lgr.

[For prepn. of  $\bar{C}$  from 4-chloro-3,5-dimethylphenol (2-chloro-*m*-5-xenol) (3:3505) by chlorination with *N*-chloroacetamide see (1)]

The nitration of  $\bar{C}$  has not been reported, and the expected 6-nitro-2,4-dichloro-3,5-dimethylphenol is unknown

[For conversion of  $\bar{C}$  to various ethers see (1).]

④ 2,4-Dichloro-3,5-dimethylphenol methyl ether: m.p. 82° (1).

④ 2,4-Dichloro-3,5-dimethylphenol ethyl ether: m.p. 53° (1).

④ 2,4-Dichloro-3,5-dimethylphenyl *p*-nitrobenzyl ether: m.p. 157° (1).

3:2182 (1) Jones, *J. Chem. Soc.* 1941, 275

### 3:2185 2,3,4-TRICHLOROPHENOL



$C_6H_3OCl_3$

Beil. VI —

VI<sub>1</sub>—

VI<sub>2</sub>—(179)

M.P. 83.5° (1) (5)

80–81° (2)

79° (3)

Nds. from pet. eth. (1) (3). — Volatile with steam (1). — Ionization const. at 25° is  $2.5 \times 10^{-8}$  (5);  $\bar{C}$  is too weakly acidic to be titrated (1) although sol. in alk.

[For prepn. from 1,2,3-trichlorobenzene (3:0990) via nitration, reduction, and use of diazo reaction see (1) (4); from barium 3-chlorophenol-6-sulfonate by hgt. with 80%  $H_2SO_4$  see (3); by chlorination of 3,4-dichlorophenol see (2).]

$\bar{C}$  treated with  $Br_2/aq.$  in excess yields on pptn. with more aq. 6-bromo-2,3,4-trichlorophenol, pl. from lt. pet., m.p. 84–85° (5).

$\bar{C}$  treated with  $(CH_3)_2SO_4 + aq. NaOH$  yields the methyl ether, 2,3,4-trichloroanisole, pr. from alc., m.p. 69.5° (3).

④ 2,3,4-Trichlorophenyl benzoate: m.p. 143° (2); 141° (4).

3:2185 (1) Tiessens, *Rec. trav. chim.* 50, 112–113 (1931). (2) Groves, Turner, Sharp, *J. Chem. Soc.* 1929, 523. (3) Hodgson, Kershaw, *J. Chem. Soc.* 1930, 1421. (4) Holleman, *Rec. trav. chim.* 39, 743 (1920). (5) Fox, Turner, *J. Chem. Soc.* 1930, 1563. (6) Tiessens, *Rec. trav. chim.* 49, 1060–1068 (1929).

### 3:2192 3,5-DICHLOROCATECHOL (3,5-Dichloropyrocatechol)



$C_6H_4O_2Cl_2$

Beil. VI — 783

VI<sub>1</sub>—

VI<sub>2</sub>—

M.P. 83–84° (1)

Colorless cryst. — Very eas. sol. hot, spar. sol. cold, aq.

[For prepn. of  $\bar{C}$  from 3,5-dichloro-2-hydroxybenzaldehyde (3,5-dichlorosalicylaldehyde) (3:2637) with  $H_2O_2$  in alk. soln. see (1)]

$\bar{C}$  reduces  $NH_4OH/AgNO_3$  (1).

$\bar{C}$  with  $FeCl_3$  gives green color turning violet on addn. of  $NaHCO_3$  (1).

— 3,5-Dichloropyrocatechol diacetate: unreported.

— 3,5-Dichloropyrocatechol dibenzoate: unreported.

3:2192 (1) Dakin, *Am. Chem. J.* 42, 455–459 (1909).



tion and use of  $\text{Cu}_2\text{Cl}_2$  reaction (1), or from 4-chloro-2,3-dimethylaniline (6-chloro-o-3-xylydine) (1) via diazotization and hydrolysis (70% yield (1)), see indic. refs.]

[For studies of bactericidal action of  $\bar{\text{C}}$  see (2) (3) (4).]

$\bar{\text{C}}$  with  $\text{Cl}_2$  in lt. pet. does not (1) give a trichloro derivative but is decomposed.

The nitration of  $\bar{\text{C}}$  has not been reported and neither of the corresp. mononitro derivs. nor the dinitro deriv. is known.

— 4-Chloro-2,3-dimethylphenyl acetate: unreported.

⑦ 4-Chloro-2,3-dimethylphenyl benzoate: m.p.  $102^\circ$  (1).

3:2218 (1) Hinkel,  
Chem. 52, 203-205  
(4) Lockemann, Hc  
2534 (1940).

(2) Heicken, Angew.  
i. 46, 296-301 (1933).  
51-71 (1939); C.A. 34,

### 3:2220 1,2,8-TRICHLORONAPHTHALENE



$\text{C}_{10}\text{H}_7\text{Cl}_3$

Beil. V-545

$\text{V}_1$ —  
 $\text{V}_2$ —

M.P.  $84^\circ$  (1)  
 $83^\circ$  (2)

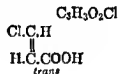
Ndls. from alc.

[For prepn. of  $\bar{\text{C}}$  from 8-chloro-1-nitronaphthalenesulfonic acid-2 [Beil. XI-187] (3), from 7,8-dichloronaphthol-1 (3:2635) (2), or from 1,2-dichloronaphthalenesulfonyl chloride-8 [Beil. XI-164] (1), each with  $\text{PCl}_5$ , see indic. refs.]

[ $\bar{\text{C}}$  treated with  $\text{ClSO}_3\text{H}$  in  $\text{CS}_2$  and prod. conv. to potassium salt yields (1) potassium 1,2,8-trichloronaphthalenesulfonate-X (corresp. sulfonyl chloride, m.p.  $105^\circ$  (1)).]

3:2220 (1) Turner, Wynno, J. Chem. Soc. 1941, 247, 252. (2) Armstrong, Wynno, Chem. News 71, 253 (1905). (3) Cleve, Chem. Ztg. 17, 398 (1903).

### 3:2240 $\beta$ -CHLOROACRYLIC ACID



Beil. II - 400  
 $\text{II}_1$ -(180)  
 $\text{II}_2$ —

M.P. *trans*  $85$ – $80^\circ$  (1)  
 $84$ – $85^\circ$  (2)  
M.P. *cis*  $63$ – $64^\circ$  (1)

[For prepn. of mixt. of *cis* and *trans* forms of  $\bar{\text{C}}$  from propiolic acid (acetylenecarboxylic acid) [Beil. II-477,  $\text{II}_1$ -(208),  $\text{II}_2$ -(449)] by htg. with conc.  $\text{HCl}$  (yield: *cis* 34%, *trans* 18% (1)) (3) (the *cis* is sepd. from *trans* by means of the lesser soly. in alc. of its potassium salt (1)), see indic. refs.; for prepn. of *trans*  $\bar{\text{C}}$  from  $\beta$ -chloropropionic acid (3:0460) by loss of  $\text{HCl}$  on passing its vapor over  $\text{BaCl}_2$  at  $280$ – $300^\circ$  see (4); from ethyl  $\beta,\beta$ -dichloropropionate with 3 moles alc.  $\text{KOH}$  see (5); from chloralide (3:3510) in alc. by protracted treatment with  $\text{Zn} + \text{HCl}$  see (2) (5).]

The *cis* isomer of  $\bar{\text{C}}$  on htg. in a s.t. at  $125^\circ$  for 15 hrs. is partially conv. (1) to the *trans* isomer.

$\bar{\text{C}}$  (both forms) readily reduces  $\text{KMnO}_4$  in the cold (1).

[ $\bar{\text{C}}$  on htg. with 5 pts. 40%  $\text{HCl}$  in s.t. at  $80$ – $85^\circ$  for 35–40 hrs. yields (5)  $\alpha,\beta$ -dichloropropionic acid (3:0855), m.p.  $56^\circ$  (5).]

[ $\bar{\text{C}}$  on esterification with  $\text{EtOH}$  yields ethyl  $\beta$ -chloroacrylate, b.p.  $143$ – $145^\circ$  (2),  $146^\circ$  (6).]

3:2240 (1) Backer, *Rec. trav. chim.* **54**, 167-170 (1935). (2) Wallach, *Ann.* **193**, 28-34 (1878). (3) Bandrowski, *Ber.* **15**, 2702 (1882). (4) I.G., French 697,311, Jan. 15, 1931; *Cent.* **1931**, I 2934. (5) Otto, *Ann.* **239**, 261-272 (1887). (6) Pinner, Bischoff, *Ann.* **179**, 88 (1875).

3:2265  $\alpha,\beta$ -DICHLOROACRYLIC ACID  $\text{C}_3\text{H}_2\text{O}_2\text{Cl}_2$  Beil. II - 401  
 $\text{CH}=\text{C}-\text{COOH}$   $\Pi_1$ -(186)  
 $\text{Cl} \quad \text{Cl}$   $\Pi_2$ —

M.P. 85-86° (1) (2) (3) (5) (6) (7) Neut. Eq. 141  
 87-88° (4)

Monoclinic (5) pr. (from  $\text{CHCl}_3$  (5)); cryst. from pet. eth. (4) or  $\text{CS}_2$  (7). — Eas. sol. aq., alc., ether (2) (4),  $\text{CHCl}_3$  (2); spar. sol. in cold (1) but eas. sol. in hot  $\text{C}_6\text{H}_6$ ,  $\text{CS}_2$  or pet. eth. (2). — Rapidly volatilizes in air (2) or on warming (4). — May be purified by melting with a little aq. (2).

Although two geom. isomers are possible only one is known.

[For prepn. from various sources see Beil. II-401, Beil.  $\Pi_1$ -(186), and (3).]

Salts:  $\text{Ag}\bar{\text{A}}$ , pptd. in fine ndls. from even dil. aq. solns. of  $\bar{\text{C}}$  on addn. of  $\text{AgNO}_3$ ; can be recrystd. from hot aq. (1) (2) (4) (6); Ag content = 43.54%;  $\text{Ba}\bar{\text{A}}_2 \cdot \text{H}_2\text{O}$ , sol. in 16 pts. cold aq. (1) (2) (4) (6);  $\text{Ca}\bar{\text{A}}_2 \cdot 3\text{H}_2\text{O}$ , extremely sol. aq., loses cryst. aq. at 80° (1) (2);  $\text{K}\bar{\text{A}}$ , quite sol. even in cold aq. but may be obtained in long slender anhyd. ndls. from conc. solns. (1) (2).

$\bar{\text{C}}$  in  $\text{CHCl}_3$  does not add  $\text{Br}_2$  (2), but  $\bar{\text{C}}$  on htg. (in s.t.) with 1 mole  $\text{Br}_2$  at 100° gives (9)  $\alpha,\beta$ -dibromo- $\alpha,\beta$ -dichloropropionic ac. [Beil. II-259], pr. from  $\text{CS}_2$  or  $\text{CHCl}_3$ , m.p. 94-95° (9).

$\bar{\text{C}}$  is not decomposed by excess hoil.  $\text{Ba}(\text{OH})_2$  (7).

$\bar{\text{C}}$  with thionyl chloride yields (7)  $\alpha,\beta$ -dichloroacrylyl chloride, b.p. 145-146°,  $n_D^{20} = 1.5288$ , which is only slowly hydrolyzed by aq. but which on cautious addn. to conc.  $\text{NH}_4\text{OH}$  yields  $\alpha,\beta$ -dichloroacrylamide, cryst. from dil. alc., m.p. 134° (7), 132° (10).

3:2265 (1) Bennett, Hill, *Ber.* **12**, 655-657 (1879). (2) Hill, *Am. Chem. J.* **3**, 167-172 (1881/2). (3) Klebansky, Wolkstein, Orłowa, *J. prakt. Chem.* **145**, 12-13 (1936). (4) Zinke, *Ber.* **24**, 918 (1891). (5) Melville, *Am. Chem. J.* **4**, 174-176 (1882/3). (6) Clamician, Silber, *Ber.* **16**, 2392 (1883). (7) Prins, *J. prakt. Chem.* (2) **89**, 420 (1914). (8) Prins, *Rec. trav. chim.* **56**, 780-781 (1937). (9) Hill, Maberry, *Ber.* **14**, 1679-1680 (1881); *Am. Chem. J.* **4**, 267-270 (1882/3). (10) Prins, *Ger.* **261,689**, July 2, 1913; *Cent.* **1913**, II 394.

3:2280 3-CHLORO-2-METHYLPHENOL  $\text{C}_7\text{H}_7\text{OCl}$  Beil. VI - 350  
 (3-Chloro-o-cresol)



M.P. 86° (1) (2) (3) B.P. 225° (2)

Long white ndls. (from aq.) (1) — Volatile with steam (2).

[For prepn. (75-86% yield) from 3-chloro-2-methylaniline [Beil. XII-836] see (1) (2); from 3-hydroxy-2-methylaniline [Beil. XIII-579] (45-50% yield) see (1).]

$\bar{\text{C}}$  on nitration (1) in  $\text{AcOH}$  with 100%  $\text{HNO}_3$  at +10° yields mixt. of equal amts. of two mononitration products: 6-nitro-3-chloro-2-methylphenol [Beil. VI-366], volatile with steam, yel. cryst. from alc., m.p. 64.5° (1), and 4-nitro-3-chloro-2-methylphenol [Beil. VI-367], not volatile with steam, cryst. from aq., m.p. 135° (1).

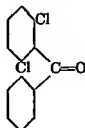
$\bar{\text{C}}$  on nitration (4) with 3 pts.  $\text{HNO}_3$  ( $D = 1.48$ ) at 0° gives a dinitro compd., 4,6-dinitro-3-chloro-2-methylphenol, long yel. ndls. from dil. alc., m.p. 82-83° (4); acetyl deriv., m.p. 95° (4).

$\bar{C}$  in alk. soln. coupled with diazotized *p*-nitroaniline yields (1) 3-chloro-2-methyl-6-(*p*-nitrobenzene-azo-)phenol [Beil. XVI-132], cryst. from 50% alc., m.p. 230°.

$\bar{C}$  in 3 pts. 20% NaOH shaken with 1 pt.  $(CH_3)_2SO_4$ , distilled with steam, gives 3-chloro-2-methylanisole [Beil. VI-359], b.p. 213.5° (2).

3:2280 (1) Noelting, *Ber.* 37, 1019-1021 (1904). (2) Ullmann, Panchaud, *Ann.* 350, 112-113 (1906). (3) Zincke, *Ann.* 417, 207 (1918). (4) Zincke, *Ann.* 417, 234-235 (1918).

3:2285 2,6-DICHLOROBENZOPHENONE  
(2,6-Dichlorophenyl phenyl  
ketone)



$C_{13}H_8OCl_2$  Beil. S.N. 652

M.P. 86° (1)

Colorless cryst. (from alc. (1)).

$\bar{C}$  does not react with the usual ketone reagents (1).

$\bar{C}$  fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (1) BzOH (1:0715) (96% yield) and *m*-dichlorobenzene (3:5960).

3:2285 (1) Lock, Rödiger, *Ber.* 72, 869 (1939).

3:2287 2,3,6-TRICHLOROBENZALDEHYDE

$C_7H_3OCl_3$

Beil. VII-238  
VII<sub>1</sub>-



M.P. 86-87° (1)

86° (2) (3)

Colorless ndls. from lgr.

[For prepn. of  $\bar{C}$  from 3-amino-2,6-dichlorobenzaldehyde by diazotization and use of  $Cu_2Cl_2$  reaction see (1) (2).]

$\bar{C}$  with  $PCl_5$  gives (81% yield (4)) 2,3,6-trichlorobenzal (di)chloride (3:2178), m.p. 83°; note that this prod. depresses m.p. of  $\bar{C}$ .

$\bar{C}$  with 50% aq. KOH at 100° for 5 hrs. under  $N_2$  undergoes cleavage of the aldehyde group giving (88% yield (3)) 1,2,4-trichlorobenzene (3:6420) and the corresp. potassium formate.

$\bar{C}$  with anhydrous NaOAc +  $Ac_2O$  on hgt. (Perkin synthesis) gives (64-68% yield (5)) 2,3,6-trichlorocinnamic acid, cryst. from AcOH, m.p. 189°.

[ $\bar{C}$  with MeMgI in dry ether, followed by usual hydrolysis, gives (85% yield (2)) methyl-2,3,6-trichlorophenyl-carbinol, m.p. 87-88°, b.p. 149-155° at 11 mm. (corresp. benzoate, m.p. 106.5°).]

— 2,3,6-Trichlorobenzaldoxime: unreported.

— 2,3,6-Trichlorobenzaldehyde phenylhydrazone: unreported.

— 2,3,6-Trichlorobenzaldehyde *p*-nitrophenylhydrazone: unreported.

— 2,3,6-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

3:2287 (1) Geigy  
(2) Lock, Böck, *B*  
62, 338 (1933).

3:2287-3:2288  
" " atsh.

## 3:2290 PENTACHLOROBENZENE



Beil. V - 205

V<sub>1</sub>-(113)V<sub>2</sub>-(157)

M.P. 87° (1) (2) B.P. 275-277° (10)

86-87° (3) (4)

86° (4) (5) (6) (7) (17)

85-86° (8) (9) (10)

85° (11) (12) (13)

84-85° (14)

84° (15) (16)

Long colorless ndls from alc.; volatile with steam; sublimes readily. — Almost insol. cold alc., apprec. sol. boilg. alc.; eas. sol. ether,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , or  $\text{CS}_2$ ; spar. sol. conc.  $\text{HNO}_3$ .

[For prepn. of  $\bar{\text{C}}$  from nonachlorobenzophenone-*o*-carboxylic acid [o-(pentachlorobenzoyl)-tetrachlorobenzoic acid] [Beil. X<sub>1</sub>-(358)] by btg with 10 pts conc.  $\text{H}_2\text{SO}_4$  at 200-250° for ½ hr. (simplest prepn. of pure  $\bar{\text{C}}$ ) see (12); for formn. of  $\bar{\text{C}}$  from 2,3,4,5,6-pentachloroacetophenone (6) or 2,3,4,5,6-pentachlorobenzophenone (11) by  $\text{KOH}/\text{NaOH}$  fusion see indic. refs., from 2,3,4,5,6-pentachlorobenzaldehyde (3:4892) (2) by htg. with 50% aq.  $\text{KOH}$  5 hrs at 100° (88% yield) see (2).]

[For prepn. of  $\bar{\text{C}}$  from 2,3,5,6-tetrachloroaniline (7) via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reactn. see (7), from 2,3,5-trichloro-*p*-phenylenediamine via tetrazotization in  $\text{AcOH}$  with nitrosylsulfuric acid and use of  $\text{Cu}_2\text{Cl}_2$  reactn. (80% yield) see (3).]

[For formn. of  $\bar{\text{C}}$  from benzene with  $\text{Cl}_2$  (7), or  $\text{Cl}_2$  + cat. (20), or  $\text{Cl}_2$  in pres. of  $\text{I}_2$  (18), or  $\text{AlCl}_3$  (19) see indic. refs.; from chlorobenzene with  $\text{Cl}_2$  +  $\text{Cu}$  at 200° see (21); from 1,3,5-trichlorobenzene (3:1400) with  $\text{Cl}_2$  +  $\text{Al}/\text{Hg}$  see (17); from all three tetrachlorobenzenes with  $\text{Cl}_2$  +  $\text{Al}/\text{Hg}$  see (17); from 1,2,4,5-tetrachlorobenzene (3:4115) in  $\text{SOCl}_2$  or  $\text{CCl}_4$  with  $\text{SO}_2\text{Cl}_2$  +  $\text{AlCl}_3$  +  $\text{S}_2\text{Cl}_2$  see (8) (note that under these circumstances *p*-dichlorobenzene (3:0980) gives a mixt. of tetra and hexachlorobenzenes (8) (22)); from lower chlorinated derivs. of benzene by btg. with  $\text{FeCl}_3$  see (5); from diphenyl sulfone with  $\text{Cl}_2$  in sunlight followed by treat. with alc.  $\text{KOH}$  see (13) (23); from tetrachlorobenzyl chloride with  $\text{Cl}_2$  see (16); from acet-*N*-nitro-2,3,5,6-tetrachloroaniline on htg. in toluene or from parent base on attempted acetylation see (15); from trichloroethylene (3:5170) at 700° see (9); from iodopentachlorobenzene with  $\text{MeOH}/\text{NaOH}$  see (11).]

[For formn. of  $\bar{\text{C}}$  from various chlorine addition products derived from *o*-dichlorobenzene (3:6055) (4), *m*-dichlorobenzene (3:5960) (4), *p*-dichlorobenzene (3:0980) (4), 1,2,4,5-tetrachlorobenzene (3:4115) (24), and even  $\bar{\text{C}}$  itself (25) see indic. refs.]

[ $\bar{\text{C}}$  with liq.  $\text{Cl}_2$  in s.t. in sunlight adds 2  $\text{Cl}_2$  with considerable sluggishness yielding (26) (25) a mixt. of two stereoisomeric nonachlorocyclohexenes.]

[ $\bar{\text{C}}$  with fuming  $\text{H}_2\text{SO}_4$  gives on protracted btg. (27) a red dyestuff, sol. in alk. with deep red color.]

[ $\bar{\text{C}}$  with  $N/2$   $\text{NaOMe}$  in  $\text{MeOH}$  in s.t. at 160° for 7½ hrs. gives (7) 2,3,5,6-tetrachlorophenol, m.p. 115° (7) (benzoate, m.p. 136° (28)), accompanied by a small amt. 2,3,4,5-tetrachlorophenol, itself not obt'd. pure but yielding (28) a benzoate of m.p. 110° (28). — [For further study of actn. of  $\text{MeOH}/\text{NaOH}$  on  $\bar{\text{C}}$  see (29) (30).]

$\bar{\text{C}}$  on nitration, e.g., with 7-8 wt. pts.  $\text{HNO}_3$  ( $D = 1.52$ ) at 100° for 1 hr. (7), gives (7) (9) (18) (31) pentachloronitrobenzene [Beil. V-247], ndls. from alc., tbls. from  $\text{CS}_2$ , m.p. 146° (9) (18) (31), 143° (7); note that since  $\bar{\text{C}}$  is spar. sol. in conc.  $\text{HNO}_3$  any unchanged material may separate with the crude prod. (31). — [This pentachloronitrobenzene with

N/10 NaOMe in MeOH boiled for 8 hrs. loses NO<sub>2</sub> instead of Cl yielding (31) methyl pentachlorophenyl ether (pentachloroanisole), m.p. 104-105° (31); cf. also under pentachlorophenol (3:4850).]

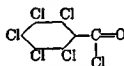
3:2290 (1) van der Linden, *Rec. trav. chim.* 55, 285 (1936). (2) Lock, *Ber.* 66, 1533 (1933). (3) Schoutissen, *J. Am. Chem. Soc.* 55, 4539-4540 (1933). (4) van der Linden, *Ber.* 45, 411-418 (1912). (5) Thomas, *Compt. rend.* 126, 1212 (1898). (6) Lock, Böck, *Ber.* 70, 925 (1937). (7) Holleman, van der Hoeven, *Rec. trav. chim.* 39, 745-746, 749 (1929). (8) Silberrad, *J. Chem. Soc.* 121, 1020-1021 (1922). (9) Nicodemus, *J. prakt. Chem.* (2) 83, 319 (1911). (10) Ladenburg, *Ann.* 172, 344 (1874).

(11) Lock, Rödiger, *Ber.* 72, 870 (1939). (12) Eckert, Steiner, *Monatsh.* 36, 183 (1915); *Ber.* 47, 2629 (1914). (13) Otto, *Ann.* 154, 185 (1870). (14) Dadieu, Pongratz, Kohlrausch, *Monatsh.* 61, 434 (1932). (15) Peters, Rowe, Stead, *J. Chem. Soc.* 1943, 372. (16) Beilstein, Kuhlberg, *Ann.* 152, 247-248 (1869). (17) Cohen, Hartley, *J. Chem. Soc.* 87, 1366 (1905). (18) Jungfleisch, *Ann. chim.* (4) 15, 283-287 (1868). (19) Mouneyrat, Pourcet, *Compt. rend.* 127, 1028 (1898). (20) Moose, Malowan (to Swann Research, Inc.), U.S. 2,019,495, Aug. 6, 1935; *Cent.* 1936, 2984; *C.A.* 29, 6330 (1935).

(21) Tei, Komatsu, *Mem. Coll. Sci., Kyoto Imp. Univ.* A-10, 325-330 (1927); *Cent.* 1928, I 2370. (22) Roberts and Co., & Silberrad, *Brit.* 193,200, March 15, 1923; *Cent.* 1925, I 904. (23) Otto, Ostrop, *Ann.* 141, 107-108 (1867). (24) van der Linden, *Rec. trav. chim.* 55, 425-427 (1936). (25) van der Linden, *Rec. trav. chim.* 55, 569-579 (1936). (26) van der Linden, *Rec. trav. chim.* 55, 322 (1936). (27) Istrati, *Bull. soc. chim.* (2) 48, 36-41 (1887). (28) Holleman, *Rec. trav. chim.* 40, 318-319 (1921). (29) de Crauw, *Rec. trav. chim.* 50, 787 (1931). (30) van der Linden, *Rec. trav. chim.* 57, 787 (1938).

(31) Berekman, Holleman, *Rec. trav. chim.* 44, 857-858 (1925).

### 3:2295 PENTACHLOROBENZOYL CHLORIDE

C<sub>7</sub>OCl<sub>6</sub>

Beil. S.N. 938

M.P. 87° (1)

Colorless tbs. from hot alc.

[For prepn. of  $\bar{C}$  from *unsym.*-tetrachlorophthalyl (di)chloride (3,3,4,5,6,7-hexachlorophthalide) [Beil. XVIII<sub>1</sub>-(484)] on htg. nt 300° in pres. of Cl<sub>2</sub> see (1).]

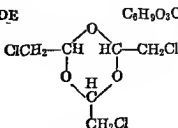
$\bar{C}$  during protracted htg. loses CO yielding (1) hexachlorobenzene (3:4939) (this type of decompn. is generally facilitated by AlCl<sub>3</sub> although in this case this aspect has not been reported).

$\bar{C}$  with MeOH on refluxing for 30 hrs. gives (1) methyl pentachlorobenzoate m.p. 97° (1); note that esterification is slow and that  $\bar{C}$  can be recrystallized from EtOH without change.

$\bar{C}$  on hydrolysis with alc. KOH, followed by acidification, yields (1) pentachlorobenzoic acid (3:4910).

3:2295 (1) Kirpal, Kunze, *Ber.* 62, 2104-2105 (1929).

### 3:2300 TRICHLOROPARALDEHYDE (Chloroacetaldehyde trimer; 2,4,6-tris-(chloromethyl)- trioxane-1,3,5)

C<sub>6</sub>H<sub>3</sub>O<sub>3</sub>Cl<sub>3</sub>Beil. XIX - 386  
XIX<sub>1</sub>-(807)

M.P. 87-87.5° cor. (1)

B.P. 142-144° at 10 mm. (2)  
140° at 10 mm. (1)

Colorless ndis. from ether; insol. aq., spar. sol. cold alc., eas. sol. hot alc. or in ether.

[For prepn. of  $\bar{C}$  from chloroacetaldehyde (3:7212) (or its hydrate) with  $\frac{1}{2}$  vol. cold conc.  $H_2SO_4$  see (1) (3) (4).]

$\bar{C}$  on distn. at ord. press. (1) (2) (3) (4) depolymerizes to monomeric chloroacetaldehyde (3:7212), b.p.  $85^\circ$ .

3:2300 (1) Natterer, *Monatsh.* **3**, 459-464 (1882). (2) Späth, *Monatsh.* **36**, 6-7 (1915). (3) Hellerich, Speidel, *Ber.* **54**, 2634-2635 (1921). (4) Lespieau, *Bull. soc. chim.* (4) **43**, 200-201 (1928).

### 3:2325 1,2,7-TRICHLORONAPHTHALENE



$C_{10}H_5Cl_3$

Beil. V - 545

$V_1$ -(263)

$V_2$ —

M.P.  $88^\circ$  also  $84^\circ$  (1) (2)

(See Text.)

$\bar{C}$  shows the double m.p. behavior indicated also for several of its isomers, e.g., 1,2,3-isomer (3:2125), 1,2,5-isomer (3:1930), 1,3,8-isomer (3:2420), 1,4,6-isomer (3:1625).

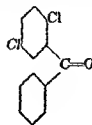
[For prepn. of  $\bar{C}$  from 1-chloro-7-sulfonaphthylamine-2 [Beil. XIV-765] via diazotization and use of  $Cu_2Cl_2$  reactn. see (1) (2); from 1,2-dichloronaphthalenesulfonyl chloride-2 [Beil. XI-184] (2) (3), from 1-chloro-7-nitronaphthalenesulfonyl chloride-2 [Beil. XI-188] (4), from 2-chloro-1-nitronaphthalenesulfonyl chloride-2 [Beil. XI-189] (5) (2), or from 1-chloronaphthalene-2,7-bis-(sulfonyl chloride) [Beil. XI-217] (2), each with  $PCl_5$  as directed, see indic. refs.]

$\bar{C}$  treated with  $ClSO_3H$  in  $CS_2$  and reactn. prod. conv. to sodium salt as directed (1) yields sodium 1,2,7-trichloronaphthalenesulfonate-X (corresp. sulfonyl chloride, m.p.  $176^\circ$  (1)).]

3:2325 (1) Turner, Wynne, *J. Chem. Soc.* **1941**, 247, 252. (2) Armstrong, Wynne, *Chem. News* **71**, 253-254 (1895). (3) Armstrong, Wynne, *Chem. News* **59**, 189 (1889). (4) Cleve, *Chem. Ztg.* **17**, 398 (1893). (5) Cleve, *Ber.* **25**, 2486-2487 (1892).

### 3:2340 2,5-DICHLOROBENZOPHENONE

(2,5-Dichlorophenyl phenyl ketone)



$C_{13}H_9OCl_2$  Beil. S.N. 652

M.P.  $88^\circ$  (1) (3)

$85-86^\circ$  (2)

Cryst. (from alc. (1)). —  $\bar{C}$  does not form a  $NaHSO_3$  epd. (1).

[For prepn. (20% yield (1)) from *p*-dichlorobenzene (3:0980) +  $BzCl$  (3:6240) +  $AlCl_3$  see (1) (2).]

$\bar{C}$  fused for 3 hrs. at  $200^\circ$  with a mixt. of  $KOH$  +  $NaOH$  gives (3) *p*-dichlorobenzene (3:0980) (65% yield (3)) and  $BzOH$  (1:0715) (91% yield (3)).

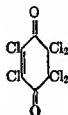
$\bar{C}$  on oxidn. with  $KMnO_4$  solu. yields (1) 2,5-dichlorobenzoic ac. (3:4340), m.p.  $150^\circ$  (1).

⊕ 2,5-Dichlorobenzophenone oxime: from  $\bar{C}$  in alc. on htg. with  $NH_2OH.HCl$  +  $BaCO_3$  for 3 days (10% yield (1)); m.p.  $135^\circ$  (on rapid htg.),  $207^\circ$  (on slow htg.) (1). [This

oxime upon Beckmann rearr. with 10 pts. conc.  $\text{H}_2\text{SO}_4$  at  $100^\circ$  for 1 hr. gives benz-2,4-dichloroanilide, m.p.  $122^\circ$  (1).]

3:2310 (1) de Crauw, *Rec. trav. chim.* 50, 767-768 (1931). (2) Ganzmüller, *J. prakt. Chem.* 138, 311-312 (1933). (3) Lock, Rödiger, *Ber.* 72, 869 (1939).

3:2360 2,3,5,5,6-HEXACHLORO-CYCLOHEXENE-2-DIONE-1,4


 $\text{C}_6\text{O}_2\text{Cl}_6$ 

Beil. VII-574  
VII<sub>1</sub>—

M.P.  $89^\circ$  (1)  
 $86-87^\circ$  (2)

B.P.  $275-285^\circ$  dec. (1)  
 $182-185^\circ$  at 45-50 mm. (1)

Cryst. (from ether/pet. ether). — Lachrymatory odor. — Eas. volatile with steam; on distn. at atm. press. dec. into chloranil (3:4978) and  $\text{Cl}_2$ . — Eas. sol. ether,  $\text{CHCl}_3$ ; fairly eas. sol. alc.,  $\text{C}_6\text{H}_6$ , lgr.; insol. aq.

[For prepn. from chloranil (3:4978) by treatment with  $\text{MnO}_2$  + conc.  $\text{HCl}$  in s.t. for 10 hrs. at  $180^\circ$  see (1); from *p*-aminophenol hydrochloride in  $\text{AcOH}$  on treatment with  $\text{Cl}_2$  see (1).]

[For use of  $\bar{\text{C}}$  as fungicide see (3).]

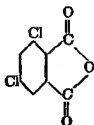
$\bar{\text{C}}$  with  $\text{KI}$  in  $\text{AcOH}$  yields (1) chloranil (3:4978). —  $\bar{\text{C}}$  on reduction with  $\text{SnCl}_2$  yields (1) tetrachlorohydroquinone (3:4941).

$\bar{\text{C}}$  on shaking with 10% aq.  $\text{NaOH}$  slowly dissolves with decompn. into dichloromaleic acid, trichloroethylene, and  $\text{HCl}$  (1).

① 3,5,5,6,6-Pentachlorocyclohexanetrione-1,2,4-anil-2 [Beil. XII-212]: in alm. 100% yield from  $\bar{\text{C}}$  (1 pt.) in  $\text{AcOH}$  (5 pts.) htd.  $\frac{1}{2}-\frac{3}{4}$  hr. at  $100^\circ$  with aniline (1 pt.), then cooling; red cryst., m.p.  $144^\circ$  (1). [This prod. is stable to conc.  $\text{HCl}$  but on stdg. with 6-8 pts. 10% aq.  $\text{NaOH}$  reacts suddenly with evoln. of ht. and odor of carbilamine; after dilution and filtration, acidification of the filtrate ppts. 1-phenyl-3,5,6-trichloropyridone-4-carboxylic acid-2 [Beil. XXII-298], m.p.  $245^\circ$  dec. (1)]

3:2360 (1) Zincke, Fuchs, *Ann.* 267, 15-24 (1892). (2) Thellacker, *Ber.* 71, 2069 (1938). (3) Ladd (to U.S. Rubber Co.), U.S. 2,362,565, Nov. 14, 1944; *C.A.* 39, 2832 (1945).

3:2375 3,5-DICHLOROPHTHALIC ANHYDRIDE


 $\text{C}_8\text{H}_2\text{O}_3\text{Cl}_2$ 

Beil. XVII-483  
XVII<sub>1</sub>—

M.P.  $89^\circ$  (1) (2)

[See also 3,5-dichlorophthalic acid (3:4580).]

Ndls. from lgr.; eas. sol. ether,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ .

[For prepn. from 3,5-dichlorophthalic acid (3:4580) by htg. AcCl (1), see indic. refs.; from 3,5-disulfophthalic acid (2) with  $\text{SOCl}_2$  at  $180^\circ$  see (2)]

$\bar{C}$  htd. with resorcinol + a drop of conc.  $H_2SO_4$ , then dislvd. in alk. and diluted, gives brilliant greenish fluorescence (1).

$\bar{C}$  with hydroquinone (1:1590) +  $AlCl_3$  +  $NnCl$  htd. at 200-220° for 40 min. gives (3) 5,7-dichloro-1,4-dihydroxyanthraquinone (5,7-dichloroquinizarin), red ndls. from xylene, m.p. 231-232° (3).]

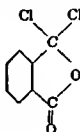
$\bar{C}$  with steam passed over cat. at 380-420° loses  $CO_2$  presumably yielding (4) 2,4-dichlorobenzoic acid (3:4560) and/or 3,5-dichlorobenzoic acid (3:4810).]

$\bar{C}$  on melting and treatment with dry  $NH_3$  gas yields (1) 3,5-dichlorophthalimide [Beil. XXI-501], yel. ndls. from hot nle., m.p. 208° (1);  $\bar{C}$  on htg. with 1 mole aniline until evolv. of gas stops gives (1) 3,5-dichlorophthalanil [Beil. XXI-501], yel. ndls. from nle., m.p. 150.0-150.5° (1).

$\bar{C}$  is insol. in cold aq. but hydrolyzes on boilg;  $\bar{C}$  on sapon. with standard alk. (Sap. Eq. = 108.5) followed by acidifn. yields 3,5-dichlorophthalic acid (3:4810) q.v.

3:2375 (1) Crossley, LeSueur, *J. Chem. Soc.* 81, 1536-1537 (1902). (2) Waldmann, Schwenk, *Ann.* 457, 293-294 (1931). (3) Waldmann, *J. prakt. Chem.* (2) 130, 99-100 (1931). (4) Jaeger (to Selden Co.), U.S. 1,004,516, June 26, 1931, *Cent.* 1931, II 3047.

3:2395 *unsym.-o-PHTHALYL*  
**DICHLORIDE**  
(*unsym.-o*-Phthaloyl dichloride;  
3,3-dichlorophthalide)



$C_8H_4O_2Cl_2$

Beil. IX - 895  
XVII<sub>1</sub>-(102)

[See also *sym.-o-phthalyl dichloride* (3:6900).]

M.P. 89° (1)  
88-89° (2)  
88.5° (3) (5)  
87-89° (4)  
84° (6)

$D_4^{20} = 1.3320$  (6)  
 $D_4^{20} = 1.351$  (5)

Prisms from  $C_6H_6$  (2), cryst. from pet. eth. (b.p. 20-50°) (4). —  $\bar{C}$  is much less reactive but far more lachrymatory (7) than *sym.-o*-phthalyl dichloride (3:6900). — The m.p. of  $\bar{C}$  is not sharp because of beginning of conversion to *sym.* isomer (4) (5), and  $\bar{C}$  shows progressive change of density when kept at 90° for 1 hr (5) —  $\bar{C}$  on distillation is converted to the *sym.* isomer and therefore shows b.p. of the latter; this change is accelerated by presence of  $AlCl_3$  or  $SnCl_4$  (1) (2) or by  $HCl$  —  $\bar{C}$  should therefore be preserved in a desiccator over soda-lime (2). — For f.p./compn. diagram of  $\bar{C}$  with its *sym.* isomer see (3); the eutectic has m.p. +8° and conts 23%  $\bar{C}$ .

[For prepn. of  $\bar{C}$  from *sym.-o*-phthalyl dichloride by htg with  $AlCl_3$  at 100° for 8-10 hrs. (72% yield) see (4).]

$\bar{C}$  in anhydrous formic acid reacts below 40° evolving  $HCl$  +  $CO$  (7) (the *sym.* isomer reacts much more readily, even below 25° (7)).

$\bar{C}$  on shaking at 0° with 10 vols. 7% aq.  $NH_4OH$  followed by acidification yields (1) (7) *o*-cyanobenzoic acid [Beil. IX-814, IX<sub>1</sub>-(365)], m.p. 190° dec., converted by htg. to phthalimide, m.p. 228.5° u.c. [Exactly this same result is obtd. with the *sym.* isomer.]

[For studies of rate of reactn. of  $\bar{C}$  with  $MeOH$  or with aniline see (2) (8).]

[For differentiation of  $\bar{C}$  from its *sym.* isomer by use of piperidinium *N*-piperidyldithiocarbamate (from piperidine + aq. +  $CS_2$ ) see (6) (7).]



3:2395 (1) Scheffer, *Ber.* 46, 2368-2369 (1913). (2) Ott, *Ann.* 392, 273-276 (1912). (3) Ott, *Ann.* 40, 21-22 (1910). (4) Ott, *Org. Syntheses Coll.* Vol. 2 (1st ed.), 528-530 (1913); (5) von Braun, Kaiser, *Ber.* 24, 1111 (1891). (6) von Braun, Kaiser, *Ber.* 24, 1111 (1891). (7) von Braun, Kaiser, *Ber.* 24, 1111 (1891). (8) Dann, Davies, Hambly,

## 3:2420 1,3,8-TRICHLORONAPHTHALENE

 $C_{10}H_5Cl_3$ 

Beil. V - 545

V<sub>1</sub>—V<sub>2</sub>—

M.P. 89.5° (1)

89° (2)

84° (1)

85° (2)

(See text.)

Ndls. from alc. in which it is eas. sol. — Note that  $\bar{C}$  (like certain of its isomers) shows a peculiar characteristic; if the fused  $\bar{C}$  in a m.p. tube is allowed to cool and withdrawn it solidifies to a translucent form which on immediate reheating shows m.p. 84-85° but if left for a time is conv. to an opaque mass which on htg. shows m.p. 89°.

[For prepn. of  $\bar{C}$  from 1-chloronaphthalene-3,8-bis-(sulfonyl chlorido) [Beil. XI-214] with  $PCl_5$  see (1) (3); from 1-nitronaphthalene [Beil. V-553, V<sub>1</sub>-(264)] with  $Cl_2$  see (4) (2).]

[ $\bar{C}$  treated with  $ClSO_3H$  in  $CS_2$  and prod. conv. to sodium salt yields (1) sodium 1,3,8-trichloronaphthalenesulfonate-5 (corresp. sulfonyl chloride, m.p. 127° (1)).]

3:2420 (1) Turner, Wynae, *J. Chem. Soc.* 1941, 247, 254. (2) Armstrong, Wynae, *Chem. News* 71, 255 (1895). (3) Armstrong, Wynae, *Chem. News* 61, 94 (1890). (4) Atterberg, *Ber.* 9, 926 (1870).

## 3:2435 1,8-DICHLORONAPHTHALENE

 $C_{10}H_8Cl_2$ 

Beil. V - 544

V<sub>1</sub>—V<sub>2</sub>-(446)

M.P. 89.0-89.5° (1)

88.5-89° (2)

88.5° (8)

88° (3) (4)

84-85° (7)

83° (5)

82.5-83.5° (11)

82° (10)

Cryst. from alc.

[For prepn. of ...]

ation and htg.

XII-1256] via diazotization and use of  $Cu_2Cl_2$ from 1,8-dinitronaphthalene [Beil. V-559, V<sub>1</sub>-(264)]

naphthalenesulfonyl chloride-1 [Beil. XI-11]

see (4); from 4,5-dichloronaphthalene

of  $-SO_3H$  group at 230° see (9) (3);[Beil. XI-182] by htg. with 1%  $H_2SO_4$

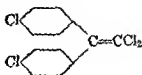
$\bar{C}$  htd. with HCl in s.t. at 250-290° rearranges (9) to 1,5-dichloronaphthalene (3:3200), m.p. 107°.

$\bar{C}$  in CS<sub>2</sub> treated with ClSO<sub>3</sub>H yields (10) 1,8-dichloronaphthalenesulfonic acid-4 [Beil. XI-162] (corresp. sulfonyl chloride, m.p. 114° (10), corresp. sulfonamide, m.p. 228° (10)).

3:2435 (1) Hampson, Weissberger, *J. Chem. Soc.* 1936, 394. (2) Weissberger, Sängewald, Hampson, *Trans. Faraday Soc.* 30, 890 (1934). (3) Cleve, *Chem. Ztg.* 17, 398 (1893). (4) Armstrong, Wynne, *Chem. News* 71, 255 (1895). (5) Atterberg, *Ber.* 9, 1732 (1876). (6) Atterberg, *Ber.* 10, 548 (1877). (7) Bergmann, Hirshberg, *J. Chem. Soc.* 1936, 334. (8) Kroll-pfeiffer, *Ann.* 430, 198 (1923). (9) Armstrong, Wynne, *Chem. News* 76, 69-70 (1897). (10) Armstrong, Wynne, *Chem. News* 61, 273-274 (1890).

(11) Woroshtzow, Koslow, *Ber.* 69, 413 (1936).

3:2438 1,1-DICHLORO-2,2-bis-(*p*-CHLOROPHENYL)-ETHYLENE



C<sub>14</sub>H<sub>8</sub>Cl<sub>4</sub> Beil. S.N. 480

M.P. 89° (1)

88-89° (2)

86-87° (3)

Colorless cryst. from alc.

[For prepn. of  $\bar{C}$  from 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane ("DDT") (3:3298) by elimination of 1 HCl with alc. KOH under reflux (1) for 10 hrs (3) or 15-20 min. (4) (yields: almost 100% (4), 81% (3)) (for study of rate see (5)), or by hgt. at 110-120° with a trace of FeCl<sub>3</sub> or AlCl<sub>3</sub> (2), see indic. refs.; for prepn. of  $\bar{C}$  from 1,1,1,2-tetrachloro-2,2-bis-(*p*-chlorophenyl)ethane (3:2477) by elimination of two adjacent chlorine atoms with Zn dust in boilg. abs. alc. refluxed 8 hrs. (66% yield) see (3)]

$\bar{C}$  on oxida. with CrO<sub>3</sub>/AcOH refluxed 4 hrs gives (100% yield (3)) 4,4'-dichlorobenzophenone (3:4270), m.p. 144° (3).

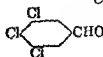
$\bar{C}$  in boilg. CHCl<sub>3</sub> contg. a little PCl<sub>5</sub> with Cl<sub>2</sub> for 3 hrs. (but without special radiation) adds 1 mole halogen giving (70% yield (3)) 1,1,1,2-tetrachloro-2,2-bis-(*p*-chlorophenyl)-ethane (3:2477), m.p. 91-92° (3).

$\bar{C}$  with KOH in ethylene glycol refluxed 10-12 hrs gives (almost 100% yield (4)) 4,4'-dichlorodiphenylmethane (3:1057) m.p. 55°; but note that  $\bar{C}$  with excess Ba(OH)<sub>2</sub>·8H<sub>2</sub>O in ethylene glycol refluxed 10-12 hrs. (4) or  $\bar{C}$  with alc. KOH in s.t. at 150-160° for 24 hrs. (7) gives (yields: 57% (7), 33% (4)) di-(*p*-chlorophenyl)acetic acid (3:4612), m.p. 166.0-166.5° u.c. (4), 163-164° (7), this acid undoubtedly being the precursor which by loss of CO<sub>2</sub> with the above KOH gives the indicated prod.

$\bar{C}$  with anhydrous AlCl<sub>3</sub> in large excess C<sub>6</sub>H<sub>6</sub> does not (6) give 1,1,2,2-tetraphenylethane (dif. from "DDT" (3:3298) q.v.).

3:2439 (1) Zeidler, *Ber.* 7, 1181 (1874). (2) Grummitt, Buck, Jenkins, *J. Am. Chem. Soc.* 67, 1 (1945). (3) U.S. Pub. Health Repts. 60, 66-71 (1945). (4) Fleck, Haller, *J. Am. Chem. Soc.* 67, 1 (1945). (5) Chem. Soc. 67, 150 (1945).

3:2440 3,4,5-TRICHLOROBENZALDEHYDE



C<sub>7</sub>H<sub>3</sub>OCls Beil. S.N. 635

M.P. 90-91° (1)

Colorless ndls. from alc. — Somewhat sol. boilg. aq.; volatile with steam. — Eas. sol. in hot alc.; also in ether, acetone,  $C_6H_6$ , or  $CHCl_3$ ; fairly sol. pet ether.

[For prepn. of  $\bar{C}$  from 4-amino-3,5-dichlorobenzaldehyde (1) by diazotization and use of  $Cu_2Cl_2$  reaction (yield of crude  $\bar{C}$  80%) see (1).]

$\bar{C}$  on oxidn. with alk.  $KMnO_4$  gives (1) 3,4,5-trichlorobenzoic acid (3:4920), m.p.  $210^\circ$ .

$\bar{C}$  on mononitration, with abs.  $HNO_3$  in cold, gives (86% yield crude (1)) 2-nitro-3,4,5-trichlorobenzaldehyde, m.p.  $118.5-119^\circ$  (corresp. phenylhydrazone, m.p.  $229^\circ$  dec.; corresp. *p*-nitrophenylhydrazone, m.p.  $293-294^\circ$  dec.; corresp. semicarbazone, m.p.  $278-279^\circ$  dec.).

— 3,4,5-Trichlorobenzaldehyde oxime: unreported.

④ 3,4,5-Trichlorobenzaldehyde phenylhydrazone: m.p.  $147^\circ$  (1).

— 3,4,5-Trichlorobenzaldehyde *p*-nitrophenylhydrazone: orange ndls. from nitrobenzene, m.p.  $342^\circ$  dec. (1).

⑤ 3,4,5-Trichlorobenzaldehyde semicarbazone: cryst. from alc., m.p.  $252-254^\circ$  (rap. htg.), but after fusion resolidifies and remelts at  $284-285^\circ$  (1).

3:2440 (1) Van de Bunt, *Rec. trav. chim.* 48, 131-137 (1929).

3:2442 5,6-DICHLORO-2,3-DIMETHYLPHENOL  
(4,5-Dichloro-*o*-3-xyleneol)



$C_6H_5OCl_2$

Beil. VI —  
VI<sub>1</sub> —  
VI<sub>2</sub> - (454)

M.P.  $90^\circ$  (1)  
 $[95^\circ$  (2)]

Cryst. from lt. pet. — Volatile with steam.

[For prepn. of  $\bar{C}$  from 5,6-dichloro-2,3-dimethylaniline (4,5-dichloro-*o*-3-xylydine) (3) via diazotization and hydrolysis (yield not stated) see (1); for formn. of  $\bar{C}$  from 4,5,6-trichloro-1,1-dimethylcyclohexen-4-one-3 with quinoline at  $170^\circ$  for 30 min. (yield not stated) see (2).]

$\bar{C}$  with  $Cl_2$  in  $CHCl_3$  does not give the expected 4,5,6-trichloro-2,3-dimethylphenol (3:4742) but instead (2) a tetrachloro deriv. (apparently containing a chlorinated methyl group), m.p.  $127.5^\circ$  (2).

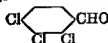
The nitration of  $\bar{C}$  has not been reported, and the expected 4-nitro-5,6-dichloro-2,3-dimethylphenol is unknown.

— 5,5-Dichloro-2,3-dimethylphenyl acetate: unreported.

④ 5,5-Dichloro-2,3-dimethylphenyl benzoate: m.p.  $133^\circ$  (1),  $128^\circ$  (2).

3:2442 (1) Hinkel, Ayling, Bevan, *J. Chem. Soc.* 1929, 2533. (2) Hinkel, *J. Chem. Soc.* 125, 1850-1851 (1924). (3) Hinkel, Ayling, Bevan, *J. Chem. Soc.* 1928, 1876-1877.

3:2445 2,3,4-TRICHLOROBENZALDEHYDE



$C_7H_3OCl_3$

Beil. VII - 238  
VII<sub>1</sub> -

M.P.  $91^\circ$  (1)  
 $90^\circ$  (2)

Ndls. from alc.

[For prepn. of  $\bar{C}$  from 2,3,4-trichlorobenzal (di)chloride (3:2212) in 58% yield by hydrolysis with fuming  $H_2SO_4$  as directed see (2).]

$\bar{C}$  on oxidn. with  $KMnO_4$  gives (1) 2,3,4-trichlorobenzoic acid (3:4810), m.p.  $186-187^\circ$ .

$\bar{C}$  with anhydr. NaOAc + Ac<sub>2</sub>O on htg. (Perkin synthesis) gives (2) 2,3,4-trichlorocinnamic acid [Beil. IX-597], m.p. 185°.

- 2,3,4-Trichlorobenzaldoxime: unreported.
- 2,3,4-Trichlorobenzaldehyde phenylhydrazone: unreported.
- 2,3,4-Trichlorobenzaldehyde *p*-nitrophenylhydrazone: unreported.
- 2,3,4-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

3:2445 (1) Nicodemus, *J. prakt. Chem.* (2) 83, 319 (1911). (2) Seelig, *Ann.* 237, 149-151 (1887).

3:2455 2,3,6-TRICHLORONAPHTHALENE



C<sub>10</sub>H<sub>7</sub>Cl<sub>3</sub> Beil. V - 546  
V<sub>1</sub>—  
V<sub>2</sub>-(446)

M.P. 91° (1)  
90.5-91° (2)

[For prepn. of  $\bar{C}$  from 3,6-dichloronaphthalenesulfonyl chloride-2 [Beil. XI-182] (1) (2), from 3-chloronaphthalene-2,7-bis-(sulfonyl chloride) [Beil. XI-217] (1) (3), or from 3-chloronaphthalene-2,6-bis-(sulfonyl chloride) [Beil. XI-216] (4), all with PCl<sub>5</sub>, see indic. refs. cf. (6).]

[For study of oxidn. of  $\bar{C}$  with CrO<sub>3</sub>/AcOH see (5).]

[ $\bar{C}$  with ClSO<sub>3</sub>H in CS<sub>2</sub> followed by conv. to salts yields a mixt. (1) derived from 2,3,6-trichloronaphthalenesulfonic acid-S (corresp. sulfonyl chloride, m.p. 118° (1)), and from 2,3,6-trichloronaphthalenesulfonic acid-X (corresp. sulfonyl chloride, m.p. 94° (1)).]

3:2453 (1) Turner, Wynne, *J. Chem. Soc.* 1941, 247, 256-257. (2) Armstrong, Wynne, *Chem. News* 61, 275 (1890). (3) Armstrong, Wynne, *Chem. News* 61, 92 (1890). (4) Armstrong, Wynne, *Chem. News* 62, 163 (1890). (5) Claus, Schmidt, *Ber.* 19, 3177-3179 (1886). (6) Franzen, Stäuble, *J. prakt. Chem.* (2) 103, 356, 377 (1921/22).

3:2460 5-CHLORO-2,4-DIMETHYLPHENOL  
(6-Chloro-*m*-4-xyleneol)



C<sub>8</sub>H<sub>9</sub>OCl Beil. VI - 488  
VI<sub>1</sub>-(242)  
VI<sub>2</sub>—

M.P. 90-91° (1) (2)

Ndls. from lgr. or aq. — Sol. hot aq. and most organic solvents. — Volatile with steam.

[For prepn. of  $\bar{C}$  from 5-chloro-2,4-dimethylaniline [Beil. XII<sub>1</sub>-486] via diazotization and hydrolysis see (1); for formn. of  $\bar{C}$  from 2,4-dimethylquinol (*m*-xyloquinol) [Beil. VIII-22, VIII<sub>1</sub>-(514)] by action of HCl (1) (2) in AcOH at 0° (1) (note that some of the isomeric 6-chloro-2,4-dimethylphenol (3:8784) is also formed) see indic. refs.]

The nitration of  $\bar{C}$  has not been reported, and none of its mononitro- or dinitro-derivatives is known.

$\bar{C}$  in alc. soln. with FeCl<sub>3</sub> gives a deep olive-green color becoming blue on dilution with aq. or reddish brown on htg. (1).

- 5-Chloro-2,4-dimethylphenyl acetate: unreported.
- ⊕ 5-Chloro-2,4-dimethylphenyl benzoate: m.p. 84.5-85.5° (1). [From  $\bar{C}$  with benzoyl chloride + aq. NaOH (1).]
- 5-Chloro-2,4-dimethylphenyl *p*-nitrobenzoate: unreported.
- 5-Chloro-2,4-dimethylphenyl *N*-phenylcarbamate: unreported.

3:2460 (1) Bamberger, Reber, *Ber.* 46, 793-803 (1913). (2) Bamberger, Reber, *Ber.* 40, 2268 (1907).

**3:2470 4-CHLOROCATECHOL**  
 (4-Chloropyrocatechol)
 $C_6H_4O_2Cl$ 
 Beil. VI - 783  
 VI<sub>1</sub>-(389)  
 VI<sub>2</sub>-(787)

M.P. 90-91° (1) (2)

88° (3)

80-81° (4)

(See also text.)

B.P. 139-139.5° at 10.5 mm. (1)

136-136.5° at 8.5 mm. (1)

Anhydrous  $\bar{C}$  exists in two forms melting at 90-91° and 59-61° (1); after fusion of the higher-melting form the resolidified  $\bar{C}$  melts 59-61° (1).

$\bar{C}$  can be recrystd. from  $C_6H_6$ ,  $CHCl_3$  from which it separates in scaly lfts., or from  $CS_2$  from which it separates in prisms. —  $\bar{C}$  cryst. from ord. ether as hemihydrate,  $\bar{C} \cdot \frac{1}{2}H_2O$ , which loses its aq. upon distn. in vac. (1). —  $\bar{C}$  is eas. sol. nq., alc., ether, AcOH, or acetone; spar. sol. lgr. (1).

[For prepn. of  $\bar{C}$  from catechol (1:1520) by action of  $SOCl_2$  see (3) (5) (1) (4); for prepn. from 5-chloro-2-hydroxybenzaldehyde (3:2800) + alk.  $H_2O_2$  see (6); for prepn. from *o*-benzoquinone [Beil. VII-600] by actn. of dry HCl in  $CHCl_3$  see (7).]

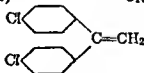
$\bar{C}$  with  $FeCl_3$  gives scarab-green color, which on addn. of  $Na_2CO_3$  becomes dark red, or with NaOAc turns blue (1).

$\bar{C}$  in AcOH treated with xanthydrol (1:5205) soon ppts. 4-chloro-5-xanthidrylcatechol, cryst. from  $C_6H_6$ , m.p. 224° (block) (8).

[For reaction with boric ac. see (2); for use in prepn. of dyestuffs see (9); for oxidn. with  $Ag_2O$  in abs. ether to 4-chlorobenzoquinone-1,2 see (1).]

④ 4-Chlorocatechol dibenzoate: from  $\bar{C}$  + BzCl in pyridine; ndls. (from ether), m.p. 96-97° (1).

3:2470 (1) Willstätter, Müller, *Ber.* 44, 2182-2181 (1911). (2) Böeseken, Mijs, *Rec.* 44, 758-760 (1925). (3) Frejka, Safranek, Zik, *Collection Czechoslov. Chem. Commun.* 6, 245 (1937). (4) Peratoner, *Gazz. chim. ital.* 28, 1 222 (1898). (5) Dakin, *Am. Chem. J.* 42, 488 (1909). (7) J (8) Fabre, *Ann. chim.* (9) 18, 114-115 (1922). 1937; *Cent.* 1938, I 187.

**3:2475 1,1-DI-(*p*-CHLOROPHENYL)-ETHYLENE**
 $C_{14}H_{10}Cl_2$ 

Beil. S.N. 480

M.P. 91° (1)

85-87° (2)

Colorless cryst. from MeOH contg. some  $C_6H_6$  (1).

[For prepn. of  $\bar{C}$  from di-(*p*-chlorophenyl)-methyl-carbinol (itself prepared from 4,4'-dichlorobenzophenone (3:4270) with  $MoMgI$ ) by dehydration see (1) (2).]

$\bar{C}$  on cat. hydrogenation gives (62% yield (4)) 1,1-di-(*p*-chlorophenyl)ethane (3:0995), m.p. 54-55°.

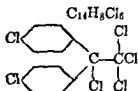
$\bar{C}$  with  $PCl_5$  in  $C_6H_6$  stood 24 hrs, then poured into nq. gives (61% yield (1))  $\beta,\beta$ -bis-(*p*-chlorophenyl)vinyl-phosphinic acid,  $(Cl.C_6H_4)_2C = CH.PO.(OH)_2$ , cryst. from AcOH, m.p. 158-159° (1).

$\bar{C}$  with  $O_3$  in  $CCl_4$  soln. in acetone/solid  $CO_2$  cooling bath, subsequently decomposed with  $H_2O_2$ , gives (2) *p*-chlorobenzoic acid (3:4949), oxalic acid (1:0445), 4,4'-dichlorobenzophenone (3:4270), and a little 4,4'-dichlorobenzophenone peroxide, cryst from acetone, m p. 217.5-218.5° (2).

[For behavior of  $\bar{C}$  with  $C_6H_6 + AlCl_3$  (3 moles) in reverse Friedel-Crafts reaction see (3)]

3:2475 (1) Bergmann, Bondi, *Ber.* 64, 1470 (1931). (2) Marvel, Nichols, *J. Org. Chem.* 6, 301 (1941). (3) Alexander, *Chem. Age* 36, 50 (1937), *Cent.* 1937, 1 4085; not in *C.A.* (4) Grummitt, Buck, Becker, *J. Am. Chem. Soc.* 67, 2265-2266 (1945).

3:2477 1,1,1,2-TETRACHLORO-2,2-bis-(*p*-CHLOROPHENYL)ETHANE



Beil, S.N. 479

M.P. 91-92° (1)

Colorless cryst. from nbs. alc.

[For prepn. of  $\bar{C}$  from 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane ("DDT") (3:3298) with  $Cl_2$  in  $CCl_4$  contg. a little  $PCl_3$  (73% yield (1)), or from 1,1-dichloro-2,2-(*p*-chlorophenyl)ethylene (3:2438) with  $Cl_2$  in  $CHCl_3$  contg. a little  $PCl_3$  (70% yield (1)), see indic. refs.]

$\bar{C}$  with Zn dust in nbs. alc. refluxed 8 hrs loses 2 chlorine atoms giving (66% yield (1)) 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (3:2438).

Despite the presence in  $\bar{C}$  of one tertiary chlorine atom,  $\bar{C}$  does not (1) react with 5% alc.  $AgNO_3$  at room temp.

$\bar{C}$  with 5% aq.  $N_2OH$  refluxed for 15 min is appreciably hydrolyzed, but with aq. alone similar treatment gives no appreciable reaction (1).

3:2477 (1) Grummitt, Buck, Jenkins, *J. Am. Chem. Soc.* 67, 155-156 (1945).

3:2480 2,3,4,6-TETRACHLOROTOLUENE



$C_7H_4Cl_4$

Beil. V - 302

V<sub>1</sub>-(153)

V<sub>2</sub>-(234)

M.P. 91.5-92° (1) (2)

92° (3)

91-92° (5)

Ndls. from alc., ether, or alc. + ether.

[For prepn. of  $\bar{C}$  from 2,4,6-trichloro-3-aminotoluene [Beil. XII-873] (1) via diazotization and use of  $Cu_2Cl_2$  reactn. (yield 92% (2)) (1) see indic. refs.; from toluene (1:7405) with  $Cl_2$  in pres. of anhydrous  $FeCl_3$  at 15-50° (90% yield) see (3) cf. (5); for formn. of  $\bar{C}$  (together with other isomers) from 2,3,4-trichlorotoluene (3:0425) or 2,4,6-trichlorotoluene (3:0380) with  $Cl_2$  in  $CCl_4$  in pres. of  $Al/Hg$  (2), or from 2,4,5-trichlorotoluene (3:2100) with  $SO_2Cl_2 + AlCl_3 + S_2Cl_2$  as directed (4), see indic. refs.]

$\bar{C}$  (1 wt. pt.) on nitration with a mixt. of 3 wt. pts.  $HNO_3$  ( $D = 1.48$ ) + 7.4 wt. pts. conc.  $H_2SO_4$  ( $D = 1.84$ ) at 105° for  $\frac{1}{2}$  hr. gives (4) 2,3,4,6-tetrachloro-5-nitrotoluene, cryst. from alc., m.p. 154° (4). — Note that the value of 131-134° reported previously (2) was undoubtedly (4) incorrect. — Note also that the m.p. of this nitration prod. is only

slightly lower than that (159°) for the corresp. prod. from 2,3,4,5-tetrachlorotoluene (3:2710).

3:2480 (1) Bures, Trpisovska, *Časopis Českoslov. Lékařnictva* 15, 179-186 (1935); *Cent.* 1936, I 1299; *C.A.* 39, 1753 (1936). (2) Cohen, Dakin, *J. Chem. Soc.* 85, 1280, 1282-1285 (1904). (3) Casella and Co., *Ger.* 282,567, April 7, 1915; *Cent.* 1915, I 862. (4) Silberrad, *J. Chem. Soc.* 127, 2082-2083 (1925). (5) Beilstein, Kuhlberg, *Ann.* 150, 287-299 (1869).

### 3:2490 1,2,4-TRICHLORONAPHTHALENE


 $C_{10}H_7Cl_3$ 
*Beil.* V - 544

 $V_1-$ 
 $V_2-$ 

M.P. 92° (1) (2)

Ndls. somewhat spar. sol. in alc. or AcOH.

[For prepn. of  $\bar{C}$  from 2,4-dichloronaphthylamine-1 (*Beil.* XII-1256) via diazotization and use of  $Cu_2Cl_2$  reactn. see (1) (3); from 2,4-dichloronaphthol-1 (3:3250) by htg. with  $PCl_5$  see (2); from 1,3-dichloronaphthalene (3:1310) with  $Cl_2$  in  $CHCl_3$  see (4).]

[ $\bar{C}$  treated with  $ClSO_3H$  in  $CS_2$  and reactn. prod. conv. to Na salt as directed (1) yields sodium 1,2,4-trichloronaphthalenesulfonate-6 (corresp. sulfonyl chloride, m.p. 158° (1)).]

3:2490 (1) Turner, Wynne, *J. Chem. Soc.* 1941, 247, 251. (2) Cleve, *Ber.* 21, 893 (1888). (3) Armstrong, Wynne, *Chem. News* 61, 273 (1890). (4) Cleve, *Ber.* 23, 954 (1890).

# CHAPTER VII

## DIVISION A. SOLIDS

(3:2500-3:2999)

### 3:2515 1,2,6-TRICHLORO-NAPHTHALENE



$C_{10}H_5Cl_3$

Beil. V - 544

V<sub>1</sub>—

V<sub>2</sub>—

M.P. 92.5° (1)  
92° (2) (8)  
91° (3)  
90° (4)

Ndls. from alc.; very eas. sol.  $CHCl_3$ .

[For prepn. of  $\bar{C}$  from 1-chloro-6-sulfonaphthylamine-2 [Beil. XIV-763] via diazotization and use of  $Cu_2Cl_2$  reactn. see (2) (5); from 1,2-dichloronaphthalenesulfonyl chloride-6 [Beil. XI-183] (6), 2-chloro-1-nitronaphthalenesulfonyl chloride-6 [Beil. XI-188] (4), 2-chloronaphthalene-1,6-bis-(sulfonyl chloride) [Beil. XI-214] (3), or 1-chloro-6-bromonaphthol-2 [Beil. VI-651] (7) by hgt. with  $PCl_5$  as directed see indic. refs.: for formn. of  $\bar{C}$  from 2,6-dichloronaphthalene (3:4040) with  $Cl_2$  in  $CHCl_3$  (9% yield) see (8).]

$\bar{C}$  treated with  $ClSO_3H$  in  $CS_2$  and prod. conv. to sodium salt yields (2) sodium 1,2,6-trichloronaphthalenesulfonate-4 (corresp. sulfonyl chloride, m.p. 184° (2)) ]

3:2515 (1) Armstrong, Wynne, *Chem. News* 71, 255 (1895). (2) Turner, Wynne, *J. Chem. Soc.* 1941, 247, 252. (3) Foralng, *Ber.* 21, 3498 (1888). (4) Cleve, *Chem. Ztg.* 17, 398 (1893). (5) Armstrong, Wynne, *Proc. Chem. Soc.* 1889, 36, 49. (6) Armstrong, Wynne, *Chem. News* 59, 189 (1889); 61, 274 (1890). (7) Armstrong, Rossiter, *Chem. News* 63, 137 (1891). (8) Wynne, *J. Chem. Soc.* 1946, 61.

### 3:2545 3-CHLORONAPHTHOL-2



$C_{10}H_7OCl$

Beil. VI —

VI<sub>1</sub>—

VI<sub>2</sub>—(603)

M.P. 93° (1)  
92° (2)  
90° (2)

Colorless ndls. from pet. ether. — Spar. sol. cold aq.; sol. hoilg. aq., and readily sol. org. solvents. — Volatile with steam; can also be distilled without decompn. but h p. is not stated (2). [The identity of the product of m.p. 63-64 5° ohtd. from supposed 3-chloronaphthyl-2 methyl ether by HI splitting (3) and regarded by its sponsors as  $\bar{C}$  is in doubt.] — Note that  $\bar{C}$  does not depress m.p. of  $\beta$ -naphthol (2).

[For prepn. of  $\bar{C}$  from 1,3-dichloronaphthol-2 (3:1990) with  $Fe(OH)_2$  htd. under press. 8 hrs. at 120° (2) or htd. in alc. with  $Zn/Cu$  couple (1) see indic. refs.; from 3-chloronaphthalene-1,2-diazoxide with alk.  $SnCl_2$  see (2); from 3-chloro-2-hydroxynaphthalenesulfonic acid-1 by hgt. with 50%  $H_2SO_4$  see (4).]



Michael, Clark, *J. prakt. Chem.* (2) **52**, 326-329 (1895). (19) Rosenmund, *Zetsche, Ber.* **51**, 583 (1918). (20) Michael, Schulthess, *J. prakt. Chem.* (2) **46**, 248-249 (1892).

(21) Kondakow, *J. Russ. Phys.-Chem. Soc.* **24**, 508 (1892). (22) Ostwald, *Z. physik. C* **3**, 264-266 (1892). (23) Michael, *J. prakt. Chem.* (2) **46**, 264-266 (1892). (24) Michael, Schulthess, *J. prakt. Chem.* (2) **46**, 254-255 (1892). (25) Michael, Schulthess, *J. prakt. Chem.* (2) **46**, 254-255 (1892). (26) Michael, Schulthess, *J. prakt. Chem.* (2) **46**, 254-255 (1892). (27) Michael, Schulthess, *J. prakt. Chem.* (2) **46**, 254-255 (1892). (28) Autenrieth, *Ber.* **29**, 1665-1666 (1916). (29) Autenrieth, *Ber.* **29**, 1665-1666 (1916). (30) Scheihler, *Topouzac* **16** (1930).

(31) Nef, *Ann.* **276**, 234 (1893). (32) Autenrieth, *Ber.* **29**, 1646-1652 (1896). (33) Backer, Beute, *Rec. trav. chim.* **54**, 559-560; 622-624 (1935). (34) Koelsch, Hochmann, LeClaire, *J. Am. Chem. Soc.* **65**, 59 (1943). (35) Bergmann, Taubadel, Weiss, *Ber.* **64**, 1501 (1931). (36) Sudborough, Roberts, *J. Chem. Soc.* **87**, 1846 (1905). (37) Michael, Oechslein, *Ber.* **42**, 322 (1909).

### 3:2635 7,8-DICHLORONAPHTHOL-1


 $C_{10}H_6OCl_2$ 

Beil. VI - 613

 VI<sub>1</sub>—

 VI<sub>2</sub>—

M.P. 95° (1) (2)

Ndls. from alc. (1) (2); rough more sol. in lgr. than isomeric 6,7-dichloronaphthol-1 (3:4315) (3).

[For prepn. from  $\beta$ -(3,4-dichlorobenzal)propionic ac. [Beil. IX-614] by distn. see (1) (2) (3);  $\bar{C}$  is separated from the larger proportion of 6,7-dichloronaphthol-1 (3:4315) by its greater soly. in lgr. (3).]

$\bar{C}$  in alk. soln. coupled with diazotized naphthionic acid (1-aminonaphthalenesulfonic acid-4) gives a dark violet color which upon acidification turns bluish cherry-red (3). [Dif. from 6,7-dichloronaphthol-1 (3:4315) q.v.]

⑦ 7,8-Dichloro-1-naphthyl acetate: cryst. from dil. alc., m.p. 87-88° (1) (2)

3:2635 (1) Armstrong, Wynne, *Chem. News* **71**, 253 (1895). (2) Armstrong, Wynne, *Proc. Chem. Soc.* **11**, 78-79 (1893); *Ber.* **29**, Referate 223-224 (1896). (3) Erdmann, Schwechten, *Ann.* **275**, 286 (1893).

### 3:2637 3,5-DICHLORO-2-HYDROXY-BENZALDEHYDE (3,5-Dichlorosalicylaldehyde)


 $C_7H_4O_2Cl_2$ 

Beil. VIII - 54

 VIII<sub>1</sub>—

M.P. 95-96° (1)

95° (2) (3)

94-95° (4)

Pale yel. scales from AcOH; insol. aq., sol. in usual org. solvents.

[For prepn. of  $\bar{C}$  from *o*-hydroxybenzaldehyde (salicylaldehyde) (1:0205) in AcOH or  $CHCl_3$  with  $Cl_2$  (2moles) (yields: 90% (3), 70% (4)) (1) see indic. refs.; for formn. from 2,4-dichlorophenol (3:0560) with hexamethylenetetramine in glycerol +  $H_3BO_3$  with  $H_2SO_4$  as directed (7% yield) see (1).]

[For study of bactericidal props. of  $\bar{C}$  see (9).]

$\bar{C}$  is sol. in dil. aq. alk. or  $NH_4OH$  yielding yel. solns.;  $\bar{C}$  is stable toward dil. aq. acids or even hot conc.  $HCl$  but with conc.  $H_2SO_4$  or  $HNO_3$  dec. on warming (2).

$\bar{C}$  in dil. aq.  $NaOH$  oxidized with dil. (3%)  $H_2O_2$  as directed yields (1) 3,5-dichloro-1,2-dihydroxybenzene (3,5-dichlorocatechol) (3:3525), pr. from cold aq., m.p. 83-84° (1)]

[ $\bar{C}$  with  $Ac_2O$  +  $NaOAc$  (Perkin condensation) yields (5) (6) 6,8-dichlorocoumarin,

cryst. from  $C_6H_6$ , m p.  $160^\circ$  (5),  $157^\circ$  (6) (this prod. on reduction with Na/Hg gives (6)  $\gamma$ -(3,5-dichloro-2-hydroxyphenyl)propionic acid (3,5-dichloromelilotic acid), m.p.  $122^\circ$  (6), on soln. in aq. alk. and boilg. with  $HgO$  or  $Hg(OAc)_2$  yields (7) 3,5-dichloro-2-hydroxycinnamic acid (3,5-dichloro-*o*-coumaric acid), cryst. from dil. alc., dec.  $242^\circ$  (7), or on oxidn. with  $KMnO_4$  gives alm. quant. yield (5) of 3,5-dichlorosalicylic acid (3:4935), m p.  $214^\circ$  (5)) —  $\bar{C}$  with  $\omega$ -(phenylacetyl)acetophenone (1,4-diphenylbutanedione-1,3) in abs. alc. with a little piperidine 7-11 hrs. at  $100^\circ$  condenses giving (16% yield (8)) 6,8-dichloro-3-phenylcoumarin, colorless ndls. from AcOH, m p.  $193-195^\circ$  (8).]

$\bar{C}$  with  $EtMgBr$  yields corresp. ter. alc., viz., 3,5-dichloro-2-hydroxyphenyl-ethylcarbinol, which at 16 mm. press. loses aq. at  $140^\circ$  giving (80% yield (4)) 2,4-dichloro-6-propenylphenol, m p.  $46-47^\circ$  (4).]

- ③ 3,5-Dichloro-2-hydroxybenzaldehyde (3,5-dichlorosalicylaldehyde): colorless ndls. from alc./aq. (4:1) (3), m.p.  $193-196^\circ$  (4),  $193^\circ$  (2). [From  $\bar{C}$  +  $NH_2OH.HCl$  in alc. on htg. 1 hr. and pouring into aq. (alm. quant. yield) (4).] [This oxime with  $Ac_2O$  on boilg. 3 hrs. gives alm. quant. yield (4) of 3,5-dichloro-2-acetoxymethylbenzotrile, colorless ndls. from alc., m p.  $78^\circ$  (4).]
- ④ 3,5-Dichloro-2-hydroxybenzaldehyde phenylhydrazone: pale yel. tpls. from alc., m p.  $153^\circ$  (4). [From  $\bar{C}$  in alc. with phenylhydrazine on shaking 10 min. (4).]
- ⑤ 3,5-Dichloro-2-hydroxybenzaldehyde semicarbazone: alm. colorless ndls. from AcOH, m p.  $227^\circ$  dec. (4). [From  $\bar{C}$  in AcOH with semicarbazide  $HCl$  in alm. quant. yield after  $\frac{1}{2}$  hr. boilg. (4).]

3:2637 (1) Dakln, *Am. Chem. J.* 42, 488-489 (1909). (2) Duff, *J. Chem. Soc.* 1911, 547-549. (3) Biltz, *Stepf. Ber.* 37, 4027-4031 (1904). (4) Clausen, *Tietze, Ann.* 449, 100 (1926). (5) Dey, *How, J. Chem. Soc.* 123, 560 (1924). (6) *Chem. Werke Grenzach A G.*, Ger. 356,019, Dec. 13, 1923; *Cent.* 1924, 1 2633. (7) Sen, Chakravarti, *J. Indian Chem. Soc.* 7, 249-250 (1930). (8) Lovett, Roberts, *J. Chem. Soc.* 1928, 1077-1078. (9) Delauney, *J. pharm. chim.* (5) 25, 254-260, 545-560 (1937), (8) 26, 177-216 (1937), *Cent.* 1938, 1 2019.

3:2638 2,6-DICHLORO-3,5-DIMETHYL-  
PHENOL  
(2,6-Dichloro-*m*-5-xyleneol)



$C_8H_6OCl_2$  Beil. S.N. 529

M.P.  $95-96^\circ$  (1)

(See also text.)

Cryst. from pet. ether. — Exs. sol.  $CHCl_3$ ,  $CCl_4$ .

[For prepn. of  $\bar{C}$  from 3,5-dimethylphenol (*m*-5-xyleneol) (1:1455) with  $SO_2Cl_2$  (2 moles) in  $CHCl_3$  see (1); note, however, that structure there assigned is 2,4-dichloro-3,5-dimethylphenol (3:2182) q.v.]

The nitration of  $\bar{C}$  has not been reported, and the expected 4-nitro-2,6-dichloro-3,5-dimethylphenol is unknown.

— 2,6-Dichloro-3,5-dimethylphenyl acetate: unreported.

— 2,6-Dichloro-3,5-dimethylphenyl benzoate: unreported.

3:2638 (1) *Lesser, Gad, Ber.* 56, 975 (1923).

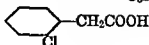
## 3:2640 2-CHLOROPHENYLACETIC

ACID

(o-Chloro- $\alpha$ -toluic acid) $C_8H_7O_2Cl$ 

Beil. IX - 447

IX-1(78)



M.P. 96°	(1)
95-96°	(2)
95°	(3) (4)
94-95°	(2)
94°	(6)
92°	(5)

Colorless ndls. from aq. [For study of ioniz. const. of  $\bar{C}$  see (1) (6) (9) (10) (13); for fate in animal body see (3); for studies of bacteriostatic props. see (11) (12).]

[For prepn. of  $\bar{C}$  from o-chlorobenzyl chloride (3:6400) via conversion to o-Cl.C<sub>6</sub>H<sub>4</sub>.CH<sub>2</sub>MgCl and subsequent carbonation with CO<sub>2</sub> see (2); from o-chlorophenylacetamide (see below) with nitrous acid see (3) (4) (6); from 2-phenyl-4-(2-chlorobenzal)oxazolone-5 (the azlactone from o-chlorobenzaldehyde + N-benzoylglycine + Ac<sub>2</sub>O (5)) [Beil. XXVII-298]] on boilg. with aq. NaOH and afterward treated with H<sub>2</sub>O<sub>2</sub> see (5).]

[For reactns. of closely related o-Cl.C<sub>6</sub>H<sub>4</sub>.CH<sub>2</sub>COOMgCl with large excess of isopropyl MgCl or C<sub>6</sub>H<sub>5</sub>MgBr yielding o-chlorophenylmalonic acid, cryst. from alc., m.p. 139° (7), see (7) (8).]

[For condens. of  $\bar{C}$  with pyrene-3-aldehyde (14) or with N-ethylcarbazole-3-aldehyde (15) in prepn. of intermediates for dyes or pharmaceuticals see indic. refs.]

[ $\bar{C}$  with PCl<sub>5</sub> yields (3) 2-chlorophenylacetyl chloride, b.p. 110-121° at 12 mm., 118-120° at 10 mm.; this prod. with aminoacetic acid (glycine) in dil. aq. alk. gives (35% yield (3)) o-chlorophenylacetaminacetic acid (o-chlorophenylaceturic acid), cryst. from hot aq., m.p. 134-135° (3).]

[ $\bar{C}$  converted to Pb salt, latter dried at 110° and distilled, yields (16) 2,2'-dichlorodibenzyl ketone, ndls. from alc., m.p. 102° (16) (oxime, m.p. 112° (16), semicarbazone, m.p. 149° (16)).] [For soly. of many other salts see (4).]

— Methyl 2-chlorophenylacetate: oil, b.p. 125-128° at 23 mm. (4). [From  $\bar{C}$  in MeOH with HCl gas (4); also from o-Cl.C<sub>6</sub>H<sub>4</sub>.CH<sub>2</sub>MgCl with methyl chloroformate in ether (2); alkaline hydrolysis gives (2)  $\bar{C}$ .]

— Ethyl 2-chlorophenylacetate: oil, h.p. 134° at 23 mm. (4). [From  $\bar{C}$  in EtOH with HCl gas (4).]

Ⓒ 2-Chlorophenylacetamide: lfts. from aq., m.p. 175° (4), 172-175° (3). [From 2-chlorophenylacetoneitrile (o-chlorobenzyl cyanide) by partial hydrol. with H<sub>2</sub>SO<sub>4</sub> (4) (3); actn. of HNO<sub>2</sub> yields  $\bar{C}$  (see above).]

Ⓒ (2-Chlorophenylacet)anilide: white ndls. from alc., m.p. 138.5° (4). [From  $\bar{C}$  + 1 mole aniline on htg. at 180-190° for 1/2 hr. (4).]

Ⓒ (2-Chlorophenylacet)-m-chloroanilide: white ndls. from dil. alc., m.p. 154° cor. (17). [From  $\bar{C}$  + m-chloroaniline (1 mole) on htg. at 180-190° for 2 hrs. (17); also from o-chlorobenzyl m-chlorophenyl ketoxime by Beckmann rearr. with PCl<sub>5</sub> in ether (17).]

Ⓒ (2-Chlorophenylacet)-p-toluidide: white ndls. from dil. alc., m.p. 169.5° (4). [From  $\bar{C}$  on htg. with 1 mole p-toluidine as for the anilide (above) (4).]

Ⓒ (2-Chlorophenylacet)phenylhydrazide: white lfts. from C<sub>6</sub>H<sub>6</sub>, m.p. 175° (4). [From  $\bar{C}$  on htg. with 1 mole phenylhydrazine (as above) (4).]

3:2649 (1) Dippy, Williams, *J. Chem. Soc.* 1934, 1888-1892. (2) Austin, Johnson, *J. Am. Chem. Soc.* 54, 657 (1932). (3) Cerecedo, Sherwin, *J. Biol. Chem.* 58, 220-222 (1923/24). (4) Mehner, *J. prakt. Chem.* (2) 62, 554-560 (1900). (5) Mauthner, *J. prakt. Chem.* (2) 95, 61 (1917). (6)



removes the aq. and yields (5) anhydrous  $\bar{C}$  (for conv. of the "hemihydrate" to anhydrous  $\bar{C}$  by use of  $\text{CaO}$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  see (12)); note, however, that anhydrous  $\bar{C}$  on stdg. in air is converted to the "hemihydrate" in less than 30 min. (11). —  $\bar{C}$  readily sublimates even at room temp. and by repeated sublimation yields (18) anhydrous form.

$\bar{C}$  has hypnotic, sedative, local anesthetic, and antiseptic characteristics and finds extensive use in medicine and in preservation of biological solns.; it has been used in treatment of nausea and seasickness, e.g., German "Nautissan" or (together with caffeine) as the British "Motherhill's Seasick Remedy" (10).

$\bar{C}$  is also employed as a modifier for cellulose acetate (13) (14) (15) (16) or cellulose ethers (17).

[For detn. of  $\bar{C}$  by complete hydrolysis with bot  $\text{MeOH/KOH}$  and subsequent detn. of chlorine by either volumetric or gravimetric methods see (3) (19).]

[For prepn. of  $\bar{C}$  from acetone (1:5400) +  $\text{CHCl}_3$  (3:5050) by addn. of dry powdered  $\text{KOH}$  (0.5 mole) below  $0^\circ$  (5) or  $2-3^\circ$  (4) or  $\text{KOH}$  in alc. as directed (11) (yields: 25% (11), 23% (5)) (2) (4) see indic. refs.; note that use of  $\text{NaOH}$  lowers the yield (5) and that  $\text{Ca(OH)}_2$  (11),  $\text{Zn(OH)}_2$  (5), or  $\text{Al(OH)}_3$  (5) yields no  $\bar{C}$ ; note also that the crude prod. contains some diacetone alcohol (1:6423) which is best removed by treatment with aq. (11) since otherwise it appears to form with  $\bar{C}$  a const.-boilg. mixt.

[For prepn. of  $\bar{C}$  from trichloroacetyl chloride (3:5420) with  $\text{MeMgI}$  in ether (4) or from ethyl trichloroacetate (3:5950) with  $\text{MeMgBr}$  in ether (20) see indic. refs.]

[ $\bar{C}$  with granulated  $\text{Zn}$  + conc.  $\text{HCl}$  (in pres. of a little ether) is reduced (21) to *tert*-butyl alc. (1:0140), m.p.  $25^\circ$ , but  $\bar{C}$  in 70% alc. warmed with  $\text{Zn}$  dust for 5 hrs. gives (4% yield (22)) 1,1-dichloro-2-methylpropene-1 (3:5300) + 1-chloro-2-methylpropene-1 (3:7120) + isobutylene (23). —  $\bar{C}$  with granulated  $\text{Zn}$  in boilg.  $\text{AcOH}$  yields (21) *tert*-butyl acetate (1:3057).]

[ $\bar{C}$  with  $\text{Na/Hg}$  in moist ether (21), or with aq. in s.t. at  $180^\circ$  for 3 hrs. (24), or  $\bar{C}$  with aq. alc.  $\text{KOH}$  (25) undergoes hydroly. of its  $-\text{CCl}_3$  group yielding  $\alpha$ -hydroxy-isobutyric acid (1:0431), m.p.  $79^\circ$ .]

Anhydrous  $\bar{C}$  in dry ether poured onto a lower layer of colorless fuchsin-aldehyde reagent (Schiff's soln.) gives a purple color (26), but this behavior is not shown by the "hemihydrate." —  $\bar{C}$  also reduces  $\text{NH}_4\text{OH/AgNO}_3$  soln. slowly in the cold (2).

[ $\bar{C}$  with cold 10% aq.  $\text{KOH}$  is claimed (27) cf. (29) to yield traces of  $\alpha$ -chloroisobutyric acid (3:0235) or carbon monoxide + acetone (28), while  $\bar{C}$  with solid  $\text{KOH}$  gives (27) methacrylic acid [Beil. II-421, II<sub>2</sub>-(398)], and  $\bar{C}$  in  $\text{MeOH}$  with alk. or tertiary org. bases, or mineral acids, yields (29) methyl methacrylate [Beil. II<sub>2</sub>-(398)].]

$\bar{C}$  with conc.  $\text{H}_2\text{SO}_4$  (10 wt. pts.) evolves  $\text{CO} + \text{CO}_2 + \text{HCl}$  (25) (26); the  $\text{CO}$  presumably results from the usual action of  $\text{H}_2\text{SO}_4$  on some  $\alpha$ -hydroxy-isobutyric acid (1:0431) first formed by hydrolysis; for the other reactions see (25).

[ $\bar{C}$  with  $\text{PCl}_5$  at  $100^\circ$  is claimed (30) (31) (21) to yield both *bis*-( $\beta,\beta,\beta$ -trichloro-*tert*-butyl) ether [Beil. I-383, I<sub>1</sub>-(193)], b.p.  $156^\circ$  (30), and 1,1,1,2-tetrachloro-2-methylpropane (3:4725), m.p. and b.p. both at  $167^\circ$  (30), but later workers (26) could obtain no reaction at all between  $\bar{C}$  and  $\text{PCl}_5$ . —  $\bar{C}$  with  $\text{PBr}_5$  at  $60^\circ$  (not above because of dissociation of  $\text{PBr}_5$ ) gives (32) cf. (21) 2,3-dibromo-1,1,1-trichloro-2-methylpropane, b.p.  $243^\circ$  (32).]

$\bar{C}$  with  $\text{P}_2\text{O}_5$  in dimethylaniline (1) or quinoline (50) btd. at  $200^\circ$  under ord. press. gives (yield: 30-43% (50), 15% (33)) 1,1,1-trichloro-2-methylpropene-2 (3:5605), b.p.  $132^\circ$ , + 57% yield of its synionic isomer 1,1,3-trichloro-2-methylpropene-1 (3:5025), h.p.  $45-46^\circ$ , accompanied by some  $\alpha$ -chloroisobutyric acid (3:0235) cf. (50).

[Various reactions of  $\bar{C}$  have been employed in prepn. of pharmaceutical prods.:  $\bar{C}$  with adipic anhydride (see text of 1:0775) at  $160-180^\circ$  for 8 hrs. (35), or  $\bar{C}$  with adipic acid (1:0775) +  $\text{SOCl}_2$  grad. htd. to  $150-160^\circ$  (36), gives  $\beta,\beta,\beta$ -trichloro-*tert*-butyl hydrogea

adipate, cryst. from pct. ether, m.p. 70° (35). —  $\bar{C}$  with 5-ethyl-5-phenyl-barbituric acid ("Luminal") does not (37) show evidence of molecular cpd. formn. but forms a eutectic, m.p. 70.4°, contg. 90%  $\bar{C}$ . —  $\bar{C}$  with 2,3-dimethyl-1-phenylpyrazolone-5 ("Antipyrine") does not (38) form a molecular cpd. but gives a eutectic contg. 60 mole %  $\bar{C}$ . —  $\bar{C}$  with 2,3-dimethyl-4-dimethylamino-1-phenylpyrazolone-5 ("Pyramidone") gives (39) a molecular cpd., m.p. 61–63°. —  $\bar{C}$  with chloral (3:5210) or chloral hydrate (3:1270) gives (40) a molecular cpd., m.p. 65°. — See also above (paragraph 4) and below (under  $\bar{C}$ 's).]

[For reactn. of  $\bar{C}$  +  $AlCl_3$  (in Friedel-Crafts sense) with benzene, toluene, and *p*-xylene see (31); for reactn. of  $\bar{C}$  with ethyl sodio-acetoacetate see (25)]

[ $\bar{C}$  with aniline in alc. KOH gives according to conditions (41) either  $\beta$  (or  $\alpha$ )-anilinoisobutyranilide [Beil. XII-558], cryst. from alc., m.p. 155–157° (41), or  $\beta$ -anilinoisobutyric acid [Beil. XII-497], cryst. from alc., m.p. 185° (41). — For study of reactions of  $\bar{C}$  with *p*-ethoxyaniline (*p*-phenetidine) + alc. KOH see (42); of  $\bar{C}$  with *o*-phenylenediamine + alc. KOH see (41)]

② Carbylamine test:  $\bar{C}$  with aniline + aq. alk. on warming gives characteristic odor of phenyl isocyanide (phenyl carbylamine).

③ Iodoform reaction:  $\bar{C}$  in aq. soln. (1/200) treated with aq. NaOH +  $I_2/KI$  soln gives yel. ppt. of iodoform (m.p. 119°) with its characteristic odor.

—  $\beta,\beta,\beta$ -Trichloro-*ter*-butyl acetate: oil, b.p. 191° (21), 190–191° (4), 151–152° at 237 mm (43). [From  $\bar{C}$  (1 pt.) with  $Ac_2O$  (2 pts.) + anhyd. NaOAc (1 pt.) refluxed 2 hrs (85% yield (43)), or from  $\bar{C}$  (1 mole) with  $AcCl$  (1 mole) under reflux (37% yield (21)).] — [Note that this ester, although unaffected by 10% aq. NaOH at 100° for 20 min. (dif. from  $\bar{C}$  which is hydrolyzed), is rapidly saponified by boilg. with 3–4 vols. conc.  $HNO_3$  for a few minutes, and upon dilution with aq. ppts.  $\bar{C}$  (43)]

④  $\beta,\beta,\beta$ -Trichloro-*ter*-butyl benzoate: cryst. from alc. upon addn. of aq., m.p. 34–35° (44) (45). [From  $\bar{C}$  with  $BzCl$  at 100° until evoln. of  $HCl$  stops (6 hrs.) (44) (45), or from  $\bar{C}$  + benzoic acid (1:0715) in pres. of  $ZnCl_2$  (45)] — [Note that this ester on boilg. with conc.  $HNO_3$  is not hydrolyzed (dif. from esters of  $\bar{C}$  with aliphatic acids, e.g., acetate (above)), but nitrated (46) yielding mainly  $\beta,\beta,\beta$ -trichloro-*ter*-butyl *m*-nitrobenzoate (see below).]

⑤  $\beta,\beta,\beta$ -Trichloro-*ter*-butyl *o*-nitrobenzoate: pl. from alc., m.p. 91° (46) (47) [From  $\bar{C}$  with *o*-nitrobenzoyl chloride on warming (46) (47).]

⑥  $\beta,\beta,\beta$ -Trichloro-*ter*-butyl *m*-nitrobenzoate: pl. from alc., m.p. 87° (46) (47). [From  $\bar{C}$  with *m*-nitrobenzoyl chloride on warming (46) (47), or from  $\beta,\beta,\beta$ -trichloro-*ter*-butyl benzoate (above) by nitration with excess conc.  $HNO_3$  below 50° (46) (47)]

⑦  $\beta,\beta,\beta$ -Trichloro-*ter*-butyl *p*-nitrobenzoate: ndls. from alc., m.p. 145° (46) (47). [From  $\bar{C}$  with *p*-nitrobenzoyl chloride on warming (46) (47).]

⑧  $\beta,\beta,\beta$ -Trichloro-*ter*-butyl 3,5-dinitrobenzoate: unreported.

—  $\beta,\beta,\beta$ -Trichloro-*ter*-butyl carbamate: pl. from  $C_6H_6$ , m.p. 102° (48) (49). [From  $\bar{C}$  with Na in  $C_6H_6$  at room temp. for 4 hrs., followed by conversion of the presumably resultant metal alcoholate with phosgene (3:5000) in toluene to  $\beta,\beta,\beta$ -trichloro-*ter*-butyl chloroformate (not isolated), and reaction of the latter in the  $C_6H_6$ /toluene soln. with dry  $NH_3$  gas (55% yield (48)) (49); note that earlier attempts (26) to obtain a metal alcoholate in toluene had led to serious explosions (cf. alkali metals with  $CHCl_3$ ) (3:5050).]

—  $\beta,\beta,\beta$ -Trichloro-*ter*-butyl *N*-phenylcarbamate: ndls. from  $C_6H_6$ , m.p. 118° (48). [From  $\bar{C}$  as in the preceding case except that aniline was used in place of  $NH_3$  in last step; yield is poor (48)]

—  $\beta,\beta,\beta$ -Trichloro-*ter*-butyl *N*-( $\alpha$ -naphthyl)carbamate: unreported.

3:2692 (1) Cameron, Holly, *J. Phys. Chem.* 2, 322-335 (1898). (2) Willgerodt, *Ber.* 14, 2451-2458 (1881). (3) Sinton, *J. Assoc. Official Agr. Chem.* 22, 730-732 (1939); 21, 557-560 (1938). (4) Taffe, *Roczniki Farmacji* 2, 99-197 (1923); *Cent.* 1924, II 304; *C.A.* 18, 2328 (1924). (5) Sah, Lei, Ma, *Sci. Repts. Natl. Tsing Hua Univ.* A-1, 209-214 (1932). (6) Perrins, *Pharm. J.* 20, 4419 (1932). (7) Smelt, *Pharm. J.* 128, 493 (1916). (8) Aldrich, *J. Biol. Chem.* 34, 263-267 (1918). (9). (10) Anon., *Chem. Ztg.* 52, 611 (1928);

*Cent.* 1928, II 1588.

(11) Flaburn, Watson, *J. Am. Pharm. Assoc.* 28, 491-493 (1939); *Cent.* 1939, II 4404; *C.A.* 33, 9283 (1939). (12) Carpenter, *Cent.* 1935, I 2256. (13) Staud, 1935; *Cent.* 1935, II 2005; *C.A.* 2 1933; *Cent.* 1934, I 2084. (15) 1,539,952, May 6, 1925; *Cent.* 1925 Brit. 195,810, May 3, 1923; *Cent.* 1924, I 719; French 562,957 1585 (1883). (19) Vastagli, *Phar* 31, 7595 (1937). (20) Henry, *Ce*

*Chem.* (2) 39, 283-289 (1880). (22) Bruyné, Davis, Gross, (23) Iocitsch, *J. Russ. Phys.-Chem. Soc.* 30, 926-924 (1898); *Cent.* 1899, I 009. (24) Willgerodt, *Ber.* 15, 2307-2308 (1882). (25) Willgerodt, Schiff, *J. prakt. Chem.* (2) 41, 516-526 (1800). (26) Wolfenstein, Loewy, Bachstez, *Ber.* 48, 2030-2019 (1916). (27) Ostropiatow, *J. Russ. Phys.-Chem. Soc.* 28, 47-59 (1896); *Ber.* 29, Referate 908-909 (1896). (28) Bressani, Segre, *Gazz. chim. ital.* 41, I 673-674 (1911). (29) Thomas, Oxley 1930; *Cent.* 1930, II 3035; *C.A.* 33, 7821 (1939). (30)

*em.* (2) 37, 365-371 (1888). (32) Swarts, *Bull. soc. chim. Bull. soc. chim.* (5) 7, 581-589 (1910); *C.A.* 36, 3507 (1912). (34) Kirmann, Jacob, *Compt. rend.* 293, 1528-1529 (1939). (35) Chem. Fabrik Dr. J. Wiernik & Co., Ger. 576,002, Oct. 19, 1934; *Cent.* 1935, I 449; *C.A.* 29, 899 (1935). (36) Chem. Fabrik Dr. J. Wiernik & Co., Ger. 583,852, April 27, 1934; *Cent.* 1934, II 283. (37) Mossini, *Boll. chim. farm.* 77, 673-674 (1938); *Cent.* 1939, I 1539; *C.A.* 33, 1875 (1939). (38) Ryeliterowna, *Wiadomości Farm.* 61, 95-97 (1934); *Cent.* 1934, II 3647; *C.A.* 28, 2983 (1934). (39) Callsen (to I.O.), Ger. 442,710, April 9, 1927; Brit. 257,816, Sept. 30, 1929; *Cent.* 1927, I

130).

1322

Soc.

923;

(47)

(18)

U.S

143).

3:2075 1,3-DICHLORO-2,2-bis(CHLORO-  
METHYL)PROPANE  $\text{C}_2\text{H}_2\text{Cl}_4$  Beil. I - 141  
(Pentaerythrityl tetrachloride)  $\text{ClCH}_2-\text{C}-\text{CH}_2\text{Cl}$  I<sub>1</sub>-  
 $\text{CH}_2\text{Cl}$  I<sub>2</sub>-(104)

M.P. 07° (1) (2) (3) (5) B.P. 110° at 12 mm. (1) (2)  
100° at 12 mm. (5)

Colorless cryst. with camphoraceous odor. — Sublimes; cas. volatile with steam. — Insol. aq.

[For prepn. of C from pentaerythritol (1:5850) with 4 moles  $\text{SOCl}_2$  + 4 moles pyridine (3) cf. (4) (5) or with conc.  $\text{HCl}$  in s.t. at 150° followed by  $\text{PCl}_3$  (2) or on htg. the trichlorohydrin (1) with  $\text{PCl}_3$  at 150° see indie. refs. (1).] [Note that pentaerythritol (1:5850) on htg. in s.t. with conc.  $\text{HCl}$  at 120-180° gives (1) a mixt. of mono-, di-, and trichloro-

hydrins: the monochlorohydrin,  $(\text{HOCH}_2)_2\text{C}\cdot\text{CH}_2\text{Cl}$ , m.p.  $141^\circ$ , b.p.  $190^\circ$  at 12 mm., is sol. in aq.; the dichlorohydrin,  $(\text{HOCH}_2)_2\text{C}(\text{CH}_2\text{Cl})_2$ , m.p.  $95^\circ$ , b.p.  $160^\circ$  at 12 mm., is sol. in aq. +  $\text{C}_6\text{H}_6$ ; the trichlorohydrin,  $\text{HOCH}_2\text{—C}\equiv(\text{CH}_2\text{Cl})_2$ , m.p.  $80^\circ$ , b.p.  $136^\circ$  at 12 mm., is sol. in  $\text{C}_6\text{H}_6$  + pet. ether (1); note also that pure dichlorohydrin has recently (6) been reported as m.p.  $79\text{--}80^\circ$ .]

3:2675 (1) Fecht, *Ber.* 40, 3888-3889 (1907). (2) Wagner, Dengel, *Z. physik. Chem.* B-16, 384 (1932). (3) Ballaus, Wagner, *Z. physik. Chem.* B-45, 173 (1939). (4) Govaert, Hansens, Beyaert, *Versl. gewone Vergadering Afdel. Naturkunde* 52, 135-137 (1943); *Cent.* 1943, II 1358; *C.A.* 38, 5201 (1944). (5) Mooradian, Cloke, *J. Am. Chem. Soc.* 67, 943 (1945). (6) Rapoport, *J. Am. Chem. Soc.* 68, 341 (1946).

### 3:2690 2-CHLORORESORCINOL


 $\text{C}_6\text{H}_4\text{O}_2\text{Cl}$ 

Beil. S.N. 554

 M.P.  $97\text{--}98^\circ$  u.c. (1)

 $04^\circ$  (2)

[See also 4-chlororesorcinol (3:3100) and 5-chlororesorcinol (3:3530).]

Colorless cryst. purified by sublimation.

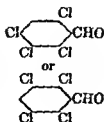
[For prepn. of  $\bar{\text{C}}$  from 2,4-dihydroxy-5-nitrobenzoic acid (5-nitro- $\beta$ -resorcylic acid) [Beil. X-382, X<sub>1</sub>-(179)] via chlorination with  $\text{SO}_2\text{Cl}_2$  in AcOH to 3-chloro-2,4-dihydroxy-5-nitrobenzoic acid, reduction of the latter with  $\text{SnCl}_2/\text{HCl}$  in AcOH to 3-chloro-2,4-dihydroxy-5-aminobenzoic acid, with final removal of the amino group by diazotization and use of alk.  $\text{SnCl}_2$ , see (1).]

( $\bar{\text{C}}$  is formed in small amt. together with 4-chlororesorcinol (3:3100) from resorcinol (1:1530) by actn. of *N,N*-dichlorourea (2).]

[Note that attempts (3) cf. (1) to prepare  $\bar{\text{C}}$  from 2-aminoresorcinol [Beil. XIII-782] by diazotization and use of Sandmeyer reactn. have failed because the actn. of nitrous acid yields 4-nitroso-2-diazo-resorcinol.]

[The prod., m.p.  $89^\circ$ , b.p.  $255\text{--}256^\circ$ , obtained (4) from resorcinol (1:1530) with  $\text{SO}_2\text{Cl}_2$  in ether may have contained  $\bar{\text{C}}$ .]

### 3:2700 2,3,4,6-(or 2,3,5,6-) TETRACHLORO-BENZALDEHYDE


 $\text{C}_7\text{H}_2\text{OCl}_4$ 

Beil. VII —

 VII<sub>1</sub>-(134)

 M.P.  $97\text{--}98^\circ$  (1)

Ndls. from pet. ether. — Eas. sol. ether,  $\text{C}_6\text{H}_6$ , or  $\text{CHCl}_3$ ; spar. sol. alc. or pet. ether; insol. aq

[For prepn. of  $\bar{\text{C}}$  from 2,3,4,6-tetrachlorobenzal (di)chloride (3:6980) by hydrolysis with conc.  $\text{H}_2\text{SO}_4$  at  $96^\circ$  see (1)]

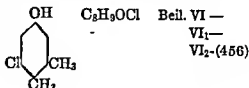


$\bar{C}$  with  $\text{NaHSO}_3$  forms the corresp. addn. cpd.; spar. sol. cold aq. (1); for use in sepn. of  $\bar{C}$  from 2,3,4,5-tetrachlorobenzaldehyde (3:3140) see (2).

[For use of  $\bar{C}$  in prepn. of dyes of the triphenylmethane series see (3).]

3:2700 (1) Cassella and Co., Ger. 290,209, Feb. 8, 1916; *Cent.* 1916, I 396-397; not in *C.A.* (2) Chem. Fabrik Criesheim Elektron, Brit. 251,511, May 27, 1926; *Cent.* 1926, II 2355; *C.A.* 21, 1361 (1927); French 603,650, April 20, 1926; *Cent.* 1926, II 2355; not in *C.A.* (3) Cassella and Co., Ger. 302,138, Nov. 28, 1917; *Cent.* 1918, I 250; not in *C.A.*

3:2705 5-CHLORO-3,4-DIMETHYLPHENOL  
(6-Chloro-*o*-4-xlenol)



M.P. 98° (1) (2)

Ndls. from lt. pet. — Volatile with steam.

[For prepn. of  $\bar{C}$  from 5-chloro-3,4-dimethylaniline (6-chloro-*o*-4-xylidine) (1) via diazotization and hydrolysis (yield not stated) see (1); from 6-amino-5-chloro-3,4-dimethylphenol (6-chloro-5-amino-*o*-4-xlenol) (2) via diazotization and elimination of original amino group using  $\text{Cu}_2\text{Cl}_2$  reaction (unusual) (yield not stated) see (2).]

$\bar{C}$  with  $\text{Cl}_2$  in  $\text{CHCl}_3$  gives (1) 2,5,6-trichloro-3,4-dimethylphenol (3:4747), m.p. 182.5°.

The nitration of  $\bar{C}$  has not been reported, and neither of the two possible mononitro derivs. nor the corresp. dinitro deriv. is known.

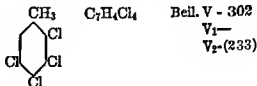
$\bar{C}$  in alk. soln. couples with benzenediazonium chloride giving (2) the corresp. azo cpd., red ndls. from alc., m.p. 143° (2).

— 5-Chloro-3,4-dimethylphenyl acetate: unreported.

Ⓐ 5-Chloro-3,4-dimethylphenyl benzoate: m.p. 42° (1).

3:2705 (1) Hinkel, *J. Chem. Soc.* 125, 1853 (1924). (2) Hinkel, Ayling, Bevan, *J. Chem. Soc.* 1928, 2532.

3:2710 2,3,4,5-TETRACHLOROTOLUENE



M.P. 98.1° cor. (1)

97-98° (2) (3)

Ndls. from  $\text{MeOH}$ .

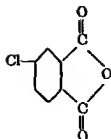
[For prepn. of  $\bar{C}$  from 3,4,5-trichloro-2-aminotoluene (3) or from 2,4,5-trichloro-3-aminotoluene [Beil. XII-872] (2) (3) via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reactn. see indic. refs.; from 3,4,5-trichlorotoluene (3:0580) with  $\text{Cl}_2$  in pres. of  $\text{Al/Hg}$  (2) (3) or with  $\text{SO}_2\text{Cl}_2$  +  $\text{AlCl}_3$  +  $\text{S}$  (35% yield (1)) see indic. refs.]

$\bar{C}$  at b.p. with  $\text{Cl}_2$  yields (4) 2,3,4,5-tetrachlorobenzal (di)chloride (3:9397).]

$\bar{C}$  on nitration with 6 pts. of a mixt. of 2 pts.  $\text{HNO}_3$  ( $D = 1.48$ ) + 4 pts.  $\text{H}_2\text{SO}_4$  ( $D = 1.84$ ) at 105° for  $\frac{1}{2}$  hr. (1) yields 2,3,4,5-tetrachloro-6-nitrotoluene, m.p. 159.6° cor. (1), 159° (3).

3:2710 (1) Silberrad, *J. Chem. Soc.* 127, 2682-5, 1280, 1285 (1904). (3) Cohen, Dakin, *J. Fabrik Griesheim-Elektron*, Brit. 251,511, May 1926, II 2355.

## 3:2725 4-CHLOROPHTHALIC ANHYDRIDE

 $C_8H_5O_3Cl$ Beil. XVII - 483  
XVII<sub>1</sub>-(253)

M.P. 98.5° (1)	B.P. 294.5° cor. at 720 mm. (6)
98° (2) (3) (4) (13)	297° (3)
97° (5)	291-295° (3)
96-97° (6)	286-290° (4)
95° (7) (8)	287° at 750 mm. (2)
90-94° (3)	

[See also 4-chlorophthalic acid (3:4390).]

Cryst. from  $CCl_4$  (5) (4), from  $Ac_2O$  (2), from ether, or from alc. (For crystallographic consts. see (2)) — Eas. sol. alc., ether,  $CHCl_3$ ; less sol.  $CS_2$ ; spar. sol. lgr.

[For use of  $\bar{C}$  with glycerol or ethylene glycol in prepn. of glyptal type resins see (26).]

[For prepn. of  $\bar{C}$  from 4-chlorophthalic acid (3:4390) by htg. or sublimation (6) (7) (8) (1) (9) or by htg. with  $AcCl$  (2) see indic. refs; from  $NaHA$  with conc.  $H_2SO_4$  at 100° see (10); from phthalic anhydride (1:0725) with  $Cl_2$  in pres. of Fe or Fe salts at 160-260° see (11) (note that crude  $\bar{C}$  obt'd. by chlorination methods or from 4-chlorophthalic acid obt'd. by chlorination methods may cont. dichlorophthalic anhydrides from which  $\bar{C}$  is separable by its greater soly. in toluene (4)); from 4-nitrophthalic anhydride [Beil. XVII-486, XVII<sub>1</sub>-(256)] with  $Cl_2$  at 240° see (12)]

[ $\bar{C}$  with  $Cl_2$  in fume  $H_2SO_4$  in pres. of  $I_2$  gives (13) mixt. contg much 3,4-dichlorophthalic anhydride (3:3695), m.p. 120-121°, b.p. 329°, and little 4,5-dichlorophthalic anhydride (3:4830), m.p. 187°.]

[ $\bar{C}$  with  $SOCl_2 + ZnCl_2$  in s.t. at 210° yields (27) 4-chlorophthalyl (di)chloride [Beil. IX-817], b.p. 275-276° (6).]

[ $\bar{C}$  in MeOH sat'd. with dry  $HCl$  yields (6) dimethyl 4-chlorophthalate, ndls. from lgr., m.p. 38° (5), m.p. 37° (6), b.p. 186-187° at 32 mm. (5);  $\bar{C}$  in EtOH similarly gives (6) diethyl 4-chlorophthalate, b.p. 173-174° at 16 mm. (14), 300-305° (6)]

$\bar{C}$  fused and treated with dry  $NH_3$  gas (6) or  $\bar{C}$  ltd. with urea (28) yields 4-chlorophthalimide [Beil. XXI-503, XXI<sub>1</sub>-(391)], m.p. 210-211° (6) (3). (Ring opening of this prod. with  $NaOCl$  yields (9) 3 pts. 4-chloro-2-aminobenzoic acid (4-chloroanthranilic acid) [Beil. XIV-365, XIV<sub>1</sub>-(518)], m.p. 235-236° (9), and 1 pt. 5-chloro-2-aminobenzoic acid as "anhydride," m.p. 178-179° (9)] [For use of 4-chlorophthalimide in prepn. of pigments of phthalocyanine type see (28).]

[ $\bar{C}$  fused with aminoacetonitrile hydrochloride or sulfate yields (15) 4-chlorophthalimidoacetamide, ndls. from hot aq., m.p. 211° (15);  $\bar{C}$  ltd. with methylenaminoacetonitrile until evoln. of  $CH_2O$  ceases yields (15) 4-chlorophthalimidoacetonitrile, ndls. from dil. AcOH, m.p. 146.5° (15);  $\bar{C}$  ltd. with glycine yields (15) 4-chlorophthalimidoacetic acid, yel. pl. from hot aq. or dil. alc., m.p. 205° (15)]

[ $\bar{C}$  with 2 moles phenol ltd. with  $ZnCl_2$  at 115-130° for 48 hrs. as directed (2) gives 76% yield phenol (di)chlorophthalcin, m.p. 214-233°, and prob. a mixt. of isomers;  $\bar{C}$  with resorcinol ltd. with trace conc.  $H_2SO_4$  yields (6) a prod. behaving as dichlorofluorescein. — Note, however, that  $\bar{C}$  with hydroquinone (1:1590) +  $AlCl_3$  +  $NaCl$  ltd. at 200-220°

(4) or  $\bar{C}$  with *p*-chlorophenol (3:0475) + fuming  $H_2SO_4 + H_3BO_3$  htd. 20 hrs. at 175-195° gives (95% yield (4)) 6-chloro-1,4-dihydroxyanthraquinone (6-chloroquinizarin), thls. from toluene, m.p. 188° (diacetate, m.p. 213°, dimethyl ether, m.p. 168.5° (4)).]

[ $\bar{C}$  with  $C_6H_5^- + AlCl_3$  yields (6) (3) 4-chloro-2-(benzoyl)benzoic acid [Beil. X-750, X<sub>1</sub>-(356)], cryst. from xylene, m.p. 180.5° (3), from  $C_6H_6$ , m.p. 170° (6) (this on ring closure with conc.  $H_2SO_4$  at 160-170° for 10 min. gives 2-chloroanthraquinone (3:4922), m.p. 204° (3). —  $\bar{C}$  with chlorobenzene (3:7903) +  $AlCl_3$  yields (3) (17) 4-chloro-2-(*p*-chlorobenzoyl)benzoic acid [Beil. X<sub>1</sub>-(357)], cryst. from xylene, m.p. 195.5° (3) (this on ring closure as above gives (3) 2,6-dichloroanthraquinone [Beil. VII-788, VII<sub>1</sub>-(413)], m.p. 278° (3)]. — For similar condensations of  $\bar{C} + AlCl_3$  with *p*-dichlorobenzene see (3), with bromobenzene see (18), with naphthalene see (25) (19); with toluene see (19) (20), with perylene see (21) (22), with 2,2'-dinaphthyl see (23).]

[For use of  $\bar{C}$  in prepn. of pigments of the phthalocyanine type see (24) (28).]

$\bar{C}$  on warming with aq. readily hydrolyzes;  $\bar{C}$  on saponification with standard alk. (Sap. Eq. = 91.3) followed by acidification yields 4-chlorophthalic acid (3:4390) q.v.

3:2725 (1) Miersch, *Ber.* 25, 2116 (1892). (2) Blicke, Smith, *J. Am. Chem. Soc.* 51, 1871-1872, 1874 (1929). (3) Egerer, Meyer, *Monatsh.* 34, 81-83, 86, 90 (1913). (4) Waldmann, *J. prakt. Chem.* (2) 126, 254-255 (1930). (5) Ayling, *J. Chem. Soc.* 1929, 255. (6) Rée, *Ann.* 233, 236-240 (1886). (7) Alén, *Bull. soc. chim.* (2) 36, 434 (1881). (8) Claus, Dehne, *Ber.* 15, 320 (1882). (9) Moore, Marrack, Proud, *J. Chem. Soc.* 119, 1788-1789 (1921). (10) Scottish Dyes, Ltd., Bangham, Thomas, *Brit.* 347,666, May 28, 1931; *Cent.* 1931, 11 1195.

(11) Dvornikoff (to Monsanto Chem. Co.), U.S. 2,028,383, Jan. 21, 1936; *Cent.* 1936, 1 2839; *C.A.* 30, 1394 (1936). (12) Imperial Chem. Ind., Ltd., Shaw, Thomas, *Brit.* 357,165, Oct. 15, 1931; *Cent.* 1931, 11 3663. (13) Villiger, *Ber.* 42, 3594 (1909). (14) von Braun, Larbig, Kredel, *Ber.* 56, 2338 (1923). (15) Stephen, *J. Chem. Soc.* 1931, 871-873. (16) Scottish Dyes, Ltd., Bangham, Hooley, Thomas, *Brit.* 339,589, Jan. 8, 1931; *Cent.* 1932, 1 2095; *C.A.* 25, 2859 (1931). (17) Müller (to I.G.), *Ger.* 405,447, April 7, 1930; *Cent.* 1931, 1 1675. (18) Waldmann, *J. prakt. Chem.* (2) 126, 74-75 (1930). (19) B.A.S.F., *Ger.* 234,917, May 26, 1911; *Cent.* 1911, 11 114. (20) B.A.S.F., *Ger.* 211,927, July 14, 1909; *Cent.* 1909, 11 396.

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3:2760  $\alpha$ -CHLOROCROTONIC ACID  $CH_3-C-H$   $C_4H_5O_2Cl$  Beil. II. - 414  
(*trans*-2-Chlorobuten-2-*oic* acid)  $Cl-C-COOH$  II<sub>1</sub>-(189)  
II<sub>2</sub>-(395)

M.P. 99.5-100° (1) (15) B.P. 212° (10) (11)  
99-100° (2) (3) 111-112° at 14 mm. (11)  
99-99.5° (6)  
99.5° (4)  
99.2° (5) (26)  
99° (7) (12) (27)  
98.5-99° (8) (11)  
97-98° (17)  
97.5° (9) (20)  
96° (10)

[See also  $\alpha$ -chloroisocrotonic acid (3:1615).]

Ndls. from aq. (4) (20) or pet. eth. (8). —  $\bar{C}$  is sol. in 47.1 pts. aq. at 19° (13); 100 pts. satd. aq. soln. at 12.5° cont. 1.97 pts.  $\bar{C}$  (9). —  $\bar{C}$  is less (9) (5) volatile with steam than the isomeric  $\alpha$ -chloroisocrotonic acid (3:1615). — Eas. sol. alc. or ether (10). — Readily sublimates (10). — Note that the m.p. of mixts. of  $\bar{C}$  with  $\beta$ -chlorocrotonic acid (3:2625) is depressed far below either (4).

[For thermal anal. of system  $\bar{C}$  + 2,6-dimethylpyrone see (12); with conc.  $H_2SO_4$  see (14).]

Preparation. \* For prepn. of  $\bar{C}$  from  $\alpha,\alpha,\beta$ -trichloro-*n*-butyric acid (3:1280) [itself readily obtd. from  $\alpha,\alpha,\beta$ -trichloro-*n*-butyraldehyde (butylchloral) (3:5910) by oxidn. with  $HNO_3$ ] by removal of two halogen atoms with Zn dust + aq. (83% yield on initial butylchloral hydrate (3)) (10), or with Zn + HCl (15), see indic. refs.; from the higher-melting form of  $\alpha,\beta$ -dichloro-*n*-butyric acid ("isocrotonic acid dichloride") (3:1903) by splitting out HCl with alc. KOH see (17) (18); from the lower-melting form of  $\alpha,\beta$ -dichloro-*n*-butyric acid ("crotonic acid dichloride") (3:1375) by splitting out HCl with excess aq. NaOH (5) (18) or with pyridine at 100° for 3 hrs. (4) or with 1%  $Am_3N$  refluxed at 160–180° for 16 hrs. (85% yield (28)) (note, however, that with NaOH the yield is low and much of the isomeric  $\alpha$ -chloroisocrotonic acid (3:1615) is formed); from  $\alpha$ -chloro- $\beta$ -hydroxy-*n*-butyric acid [Beil. III-309, 310] by elimination of  $H_2O$  with warm 80%  $H_2SO_4$  see (17) ]

[For prepn. of  $\bar{C}$  from  $\alpha,\alpha,\beta$ -trichloro-*n*-butyraldehyde (butylchloral) (3:5910) by simultaneous oxidn. and elimination of HCl with aq.  $K_4Fe(CN)_6$  (yield 44.3% (3)) (19) see indic. refs.]

[For formn. of  $\bar{C}$  from crotonic acid (1:0425) by actn. of  $Cl_2$  and distillation of product see (20); from  $\alpha$ -chloroisocrotonic acid (3:1615) by hgt. in s.t. at 150–160° for 12 hrs. (21), with pyridine HCl in pyridine 7 days at room temp (4), or to small extent even on steam distn. (22) see indic. refs.; from the methyl, ethyl, or *n*-propyl esters of  $\alpha$ -chloro- $\alpha$ -vinylacetic acid or from  $\alpha$ -chloro- $\alpha$ -vinylacetonitrile (or amide) on hydrolysis with alkali (note shift of double bond from  $\beta,\gamma$  to  $\alpha,\beta$  position) see (11); from ethyl  $\alpha$ -chlorocrotonate (3:8523) by hydrolysis with conc. HCl see (23).]

Chemical behavior. [ $\bar{C}$  on reduction with Na/Hg is dehalogenated yielding (10) crotonic acid (1:0425), m.p. 72°; note, however, that  $\bar{C}$  does not readily absorb  $H_2$  even in pres. of Pt black (11).]

$\bar{C}$  with  $Cl_2$  in  $CS_2$  adds 1 mole halogen yielding (24)  $\alpha,\alpha,\beta$ -trichloro-*n*-butyric acid (3:1280), m.p. 59.5–60°. —  $\bar{C}$  adds  $Br_2$  readily (15) yielding (10)  $\alpha,\beta$ -dibromo- $\alpha$ -chloro-*n*-butyric acid [Beil. II-286], m.p. 92° (10).

$\bar{C}$  with fuming HCl in s.t. at 100° for 5 hrs. adds 1 HCl to double bond yielding (17) (18) the higher-melting  $\alpha,\beta$ -dichloro-*n*-butyric acid (3:1903), m.p. 78°.

$\bar{C}$  behaves as a monobasic acid; dissociation const. at 25° is  $7.2 \times 10^{-4}$  (25); Neut. Eq. 120.5.

[Salts:  $NH_4\bar{A}$ , lfts. or hexag. tbs., sublimable (10);  $Na\bar{A}$  (10);  $K\bar{A}$ , lfts. from alc. in which it is spar. sol. (1 pt.  $K\bar{A}$  in 736.4 pts. 99% alc. at 16.5° (5)) (use in sepn. of  $\bar{C}$  from the isomeric  $\alpha$ -chloroisocrotonic acid (3:1615) (4) (18) (17));  $Ag\bar{A}$ , ndls., spar. sol. aq. (10) (17);  $Ca\bar{A}_2$ , pr. spar. sol. cold aq. (10) (17);  $Ba\bar{A}_2$ , more sol. aq. than  $Ca\bar{A}_2$  (10) (17);  $Cu\bar{A}_2$ , blue ndls., converted by warm aq. to a basic salt (10);  $Pb\bar{A}_2 \cdot H_2O$  (10).]

[ $\bar{C}$  with NaOEt is unchanged even at 215° (20), but  $\bar{C}$  with 10 N KOH at 190–200° decomposes with formn. of AcOH (1:1010), oxalic acid (1:0445),  $CO_2$  +  $H_2$  + other prods. (20) ]

[For study of rate of reactn. of  $\bar{C}$  with  $K_2AsO_3$  see (2) ]

[ $\bar{C}$  with  $PCl_5$  on warming gives (10)  $\alpha$ -chlorocrotonoyl chloride, liq. with sharp odor, b.p. 112° (10).]

— Methyl  $\alpha$ -chlorocrotonate: b.p. 161–162° (see 3:5870). [For study of rate of esterification of  $\bar{C}$  with MeOH see (26) (27).]

— Ethyl  $\alpha$ -chlorocrotonate: b.p. 176° (see 3:8523).

①  $\alpha$ -Chlorocrotonamide: lftn., spar. sol. cold aq., eas. sol. alc.; m.p. 113.5° (8), 111.5–112.5° (11), 107° (10). [From  $\alpha$ -chlorocrotonyl chloride (above) (10) or ethyl  $\alpha$ -chlorocrotonate (11) with conc. aq.  $NH_4OH$ ; also by other routes such as from  $\alpha,\alpha,\beta$ -trichloro-*n*-butyraldehyde (3:5910) with  $NH_4OH + KCN$  (93% yield (8)).]

—  $\alpha$ -Chlorocrotonanilide: unreported.

—  $\alpha$ -Chlorocroton- $\alpha$ -naphthalide: unreported.

3:2766 (1) Stelling, *Z. physik. Chem.* B-24, 423 (1934). (2) Backer, van Oort, *Rec. trav. chim.* 59, 57–58 (1940). (3) Roberts, *J. Chem. Soc.* 1638, 770 (1934). (4) Wallach, *Ber.* 3015–3016 (1910). (5) Wislicenus, *Ann.* 248, 288, 293, 1008–1019 (1887). (7) von Auwers, *Ber.* 56, 724 (1923).

1929, 1016. (9) Kahlbaum, *Ber.* 12, 2338–2339 (1879).

(11) Rambaud, *Bull. soc. chim.* (6) 1, 1352–1355 (1934)

1232 (1914). (13) Michael, Browne, *Am. Chem. J.* 9, 2

*J. Am. Chem. Soc.* 36, 2505 (1914). (15) Krämer, Pinner, *Ann.* 158, 51 (1871). (16) Pinner,

*Ber.* 8, 1563 (1875). (17) Melikoff, *Ann.* 234, 200, 293–204 (1886). (18) Michael, Schulthess,

*J. prakt. Chem.* (2) 46, 256, 260–262 (1892). (19) Wallach, *Ber.* 19, 1539 (1877). (20) Friedrich,

*Ann.* 219, 351–356, 371–373 (1883).

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(1888). (23) Wallach, *Ann.* 173, 391 (1874). (24) Valentin, *Ber.* 28, 2661–2662 (1895). (25)

Ostwald, *Z. physik. Chem.* 3, 244 (1889). (26) Sudborough, Roberts, *J. Chem. Soc.* 87, 1815–

1846 (1905). (27) Michael, Oechsli, *Ber.* 42, 322 (1909). (28) Long (to Wingfoot Corp.).

U.S. 2,370,067, May 15, 1945; C.A. 39, 3559 (1915).

**3:2800 5-CHLORO-2-HYDROXY-  
BENZALDEHYDE**  
(5-Chlorosalicylaldehyde)



$C_7H_5O_2Cl$

Beil. VIII-53  
VIII-1—

M.P. 100° (1)  
99.5° (2) (3) (4)  
(5) (11)  
99° (6) (7)  
98° (8)  
95–97° u.c. (9)

B.P. 105° at 12 mm. (1)

Colorless tbls. from alc.; long flat ndks. from  $C_6H_6$  (1). — Insol. aq.; sol. alc., ether. — Sol. in alk. with yel. color.

[For prepn. of  $\bar{C}$  from salicylaldehyde (1:0205) by chlorination with  $Cl_2$  (10) (11) in AcOH (2), or with  $SO_2Cl_2$  (1) (8), see indicated refs.; from 5-chloro-2-hydroxybenzyl alcohol by oxidn. with  $K_2Cr_2O_7 + H_2SO_4$  see (6); from 5-chlorosalicylic acid (3:4705) by reduction (poor yield) see (3); from *p*-chlorophenol (3:0176) via Reimer-Tiemann reactn. (4) or via hexamethylenetetramine (7) see indicated refs.]

$\bar{C}$  on reduction with Raney Ni (Al/Ni alloy) in 10% aq. alk. at 90° gives (75% yield (10)) *o*-cresol (1:1400).

$\bar{C}$  on oxidn. with  $CrO_3$  gives (in poor yield (1)) 5-chlorosalicylic ac. (3:4705), m.p. 172° (1).

$\bar{C}$  yields with satd. aq.  $NaHSO_3$  soln. a cpd.  $\bar{C}.NaHSO_3$  (12) (use in purification of  $\bar{C}$  (4)). —  $\bar{C}$  with  $NH_3$  gives 5,5',5''-trichloro-hydroxysalicylamide, yel. scales from ether, m.p. unrecorded (10). —  $\bar{C}$  in alk. gives on oxidn. with  $H_2O_2$  good yield (13) of 4-chloropyrocatechol (3:2470).

$\bar{C}$  in AcOH treated with conc.  $HNO_3$  as directed (14) gives 5-chloro-3(?)-nitrosalicylaldehyde, yel. ndls. from et. pet., m.p. 105–107° (14)

$\bar{C}$  htd. with chloroacetic ac. (3:1370) and slightly more than 2 moles KOH in s.t. at 160° yields (15) 4-chlorocoumarone (oil, volatile with steam) and 5-chloro-2-formylphenoxyacetic ac. (not volatile with steam from alk. soln.), cryst. from aq., m.p. 169–170° (15).

⑤ 5-Chlorosalicylaldoxime: ndls. from aq., m.p. 128° (15) (7); 123–124° (9); 122° (11) (6) [use in inorganic analysis (9)].

⑤ 5-Chlorosalicylaldehyde phenylhydrazine [Beil. XV-189]: m.p. 150–152° (15), 148° (11).

— 5-Chlorosalicylaldehyde *p*-nitrophenylhydrazine: unreported.

— 5-Chlorosalicylaldehyde 2,4-dinitrophenylhydrazine: unreported.

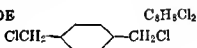
⑤ 5-Chlorosalicylaldehyde semicarbazone: ndls. from AcOH, m.p. 286–287° (11) (4)

3:2800 (1) Durrans, *J. Chem. Soc.* 123, 1426 (1923) (2) Bradley, Dains, *Am. Chem. J.* 14, 295 (1892). (3) Weil, Traun, *Monat. Ber.* 55, 2665 (1922). (4) Sen, Ray, *J. Indian Chem. Soc.* 9, 170 (1932). (5) Hanus, *J. prakt. Chem.* 158, 265 (1941) (6) Visser, *Arch. Pharm.* 235, 547 (1897) (7) Duff, *J. Chem. Soc.* 1911, 547–550. (8) Peratoner, *Gazz. chim. ital.* 28, 1, 235 (1898) (9) Flagg, Furman, *Ind. Eng. Chem., Anal. Ed.* 12, 529–531 (1940). (10) Piria, *Ann.* 30, 169 (1839).

(11) Biltz, *Stepf. Ber.* 37, 4924 (1904) (12) Bertagnani, *Ann.* 85, 196 (1853). (13) Dakin, *Am. Chem. J.* 42, 488 (1909). (14) Lovett, Roberts, *J. Chem. Soc.* 1928, 1978. (15) Stoermer, *Ann.* 312, 325–326 (1900). (16) Schwenk, Papa, Whitman, Ginsberg, *J. Org. Chem.* 9, 1–8 (1944).

### 3:2825 *p*-XYLYLENE DICHLORIDE

( $\omega, \omega'$ -Dichloro-*p*-xylene)



$C_8H_8Cl_2$

Beil. V - 384

V<sub>1</sub>-(186)

V<sub>2</sub>-(300)

M.P. 100° (1) (2)

98–99° (3)

98–100° (6)

B.P. 240–245° dec. (2)

135° at 16 mm. (1)

Lfts. or tbls. (from alc.). — Volatile with steam.

[For prepn. from *p*-xylylene glycol by distn. with conc. HCl see (4); for prepn. from benzyl chloride (3:8535) + trioxymethylene +  $ZnCl_2$  see (1) (42% yield (6)); for prepn. of  $\bar{C}$  from *p*-xylene (1:7415) with  $SO_2Cl_2$  +  $Br_2O_2$  refluxed in sunlight 4 hrs. (58% yield) see (6).]

$\bar{C}$  on htg. with 30 pts. aq. in s.t. at 170–180° yields (1) (4) *p*-xylylene glycol [Beil. VI-919], ndls., very sol. aq., alc. or ether, m.p. 112–113°.

$\bar{C}$  boiled with  $Ph(NO_2)_2$  soln. yields (5) terephthalaldehyde [Beil. VII-675], fine ndls. from boilg. aq., m.p. 115°.

$\bar{C}$  htd. with benzyl alc. (1:6480) + KOH gives good yield (1) of *p*-xylylene glycol dibenzyl ether, cryst. from alc., m.p. 67° (1).

3:2825-11-1

— 229 (1934) (2) Lauth, Grimaux, *Bull. soc. chim.*

(3) Wislicenus, Penndorf, *Ber.* 43, 1838 (1910).

Grimaux, *Compt. rend.* 83, 825 (1876). (6) Kulka,

3:2855 2,3-DICHLOROBENZO-  
QUINONE-1,4  
(*o*-Dichlorobenzoquinone)



Beil VII-632  
VII—

M.P. 100–101° (1)  
96–98° (2)  
96° (3)  
95–96° (4)

[See also 2,3-dichlorohydroquinone (3:4220).]

Yel. ndls. from aq. (2) or alc. (1). —  $\bar{C}$  has characteristic quinone odor.

[For prepn. of  $\bar{C}$  from 2,3-dichlorohydroquinone (3:4220) by oxidn. with  $MnO_2$  +  $\Delta$ ,  $H_2SO_4$  (yields: 88% (1), 60% (3)) (4), or with  $CrO_2/ArOH$  (2) see indic. refs.; for formn. of  $\bar{C}$  from *p*-benzoquinone (1:9025) in  $HCl$  or  $H_3PO_4$  with  $Cl_2$  see (5).]

[For study of oxidn.-reductn. potential of system  $\bar{C}$  + 2,3-dichlorohydroquinone (3:4220) see (1) (5).]

[ $\bar{C}$  with butadiene-1,3 gives an adduct which upon oxidn. yields (7) 2,3-dichloronaphthoquinone-1,4 (3:4857); similarly  $\bar{C}$  with 2,3-dimethylbutadiene-1,3 gives an adduct which upon oxidn. yields (7) 2,3-dichloro-6,7-dimethylnaphthoquinone-1,4.]

[For use of  $\bar{C}$  as accelerator for vulcanization of rubber see (5).]

[ $\bar{C}$  in alc. with *p*-nitrosodimethylaniline gives (60% yield (9)) corresp. nitrone; for condens. of  $\bar{C}$  with other nitroso epds. and use of prods. as dye intermediates see (10).]

[ $\bar{C}$  in  $CHCl_3$  with  $Cl_2$  is not attacked at low temps., but at ord. temp. yields (4) tetrachloro-*p*-benzoquinone (chloranil) (3:4978).]

$\bar{C}$  on reductn. (presumably with  $SO_2$  +  $H_2O$ ) yields 2,3-dichlorohydroquinone (3:4220) q.v.

3:2855 (1) Conant, Fieser, *J. Am. Chem. Soc.* 45, 2204–2205 (1923). (2) Eckert, Eder, *J. prakt. Chem.* (2) 104, 82 (1922). (3) Peratoner, Genco, *Gazz. chim. Ital.* 24, II 375–396 (1894). (4) Oliveri-Tortorelli, *Gazz. chim. Ital.* 27, II 554–555 (1897). (5) Kvalnes, *J. Am. Chem. Soc.* 56, 668–669 (1934). (6) Chelintsev, *Compt. rend. acad. sci. (U.S.S.R.)* 14, 289–291 (1937); *Cent.* 1937, II 351; *C.A.* 31, 7350 (1937). (7) L.G., *Brit.* 324,061, Feb. 27, 1930; French 677,226, March 6, 1930; French 677,781, March 14, 1930; *Cent.* 1930, II 810. (8) Fisher (to Nacagatuck Chem. Co.), French 740,978, Feb. 3, 1933; *Cent.* 1933, I 3133. (9) Gündel, Pummerer, *Ann.* 529, 31 (1937). (10) Gündel (to L.G.), *Ger.* 563,968, Nov. 11, 1932; *Cent.* 1933, II 619.

3:2885 3,4,5-TRICHLOROPHENOL



Beil VI —  
VI—  
VI<sub>2</sub>—(181)

M.P. 101° (1) (4) B.P. 271–277° u.c. at 746 mm. (3)  
99–100° (2)  
91° (3)

Ndls. from lgr. — Volatile with steam. — Ionization const. at 25° is  $4.5 \times 10^{-9}$  (4);  $\bar{C}$  is too weakly acidic to be titrated (1) although sol. in alk.

[For prepn. from 3,4,5-trichloroaniline via diazo react. (51% yield) see (1) (2); by cleavage of 3,4,5-trichloroanisole see (3).]

$\bar{C}$  treated with large excess  $Br_2$  yields 2,6-dibromo-3,4,5-trichlorophenol, ndls. from AcOH, m.p. 180° (3).

The methyl ether of  $\bar{C}$ , 3,4,5-trichloroanisole, prepared indirectly, has m.p. 63° (3).

⑤ 3,4,5-Trichlorophenyl benzoate: from  $\bar{C}$  + BzCl + 20% NaOH; ndls. from alc., m.p. 120° (3).

3:2885 (1) Tiessens, *Rec. trav. chim.* 50, 113 (1931) (2) Herzberg, Scharfenberg, *Ger.* 367,362, Jan. 20, 1923, *Cent.* 1923, II 1254. (3) Kohn, Kramer, *Monatsh.* 49, 163-165 (1928). (4) Tiessens, *Rec. trav. chim.* 48, 1068-1068 (1929).

3:2910 4,5-DICHLORO-2-METHYLPHENOL  
(4,5-Dichloro-*o*-cresol)



$C_7H_5OCl_2$

Beil. VI —

VI<sub>1</sub>-(174)

VI<sub>2</sub>-(333)

M.P. 191° (1)

Ndls. from pet. ether; spar. sol. pet. ether, eas. sol. alc., AcOH,  $C_6H_6$ .

[For prepn. of  $\bar{C}$  from 4-chloro-2-methylphenol (3:9780) with  $Cl_2$  in  $CHCl_3$  see (1).]

$\bar{C}$  in 2 pts. ice-cold  $HNO_3$  ( $D = 1.48$ ) stood for 12 hrs. gives (75% yield (1)) a prod. of compn.  $C_7H_5O_3N_3Cl_2$ , white ndls. from dry ether by addn. of pet. ether, m.p. 110° dec. (1).

$\bar{C}$  in AcOH on mononitration yields (1) 4,5-dichloro-6-nitro-2-methylphenol [Beil. VI<sub>1</sub>-(179)], yel. ndls. from pet. ether, m.p. 69° (1)

⑤ 4,5-Dichloro-2-methylphenyl benzoate: ndls. from  $C_6H_6$ , m.p. 80-81° (1). [From  $\bar{C}$  in alk. soln. on shaking with benzoyl chloride (1).]

3:2910 (1) Zincke, *Ann.* 417, 207, 231-233 (1918).

3:2935 2,3-DICHLORONAPHTHOL-1



$C_{10}H_6OCl_2$

Beil. VI-612

VI<sub>1</sub>—

VI<sub>2</sub>—

M.P. 101° (1)

Subl. in ndls.; spar. sol. cold aq., mod. sol. hot aq.; eas. sol. alc., ether, AcOH,  $CHCl_3$ ,  $C_6H_6$ .

[For prepn. from sodium 1-naphtholsulfonate-2 by htg. with  $PCl_5$  at 100-120° see (1).]

$\bar{C}$  dis. in hot  $Na_2CO_3$  yielding sol. Na salt.

$\bar{C}$  htd. with  $PCl_5$  at 130-140° yields 1,2,3-trichloronaphthalene (3:2125), colorless ndls. from alc, m.p. 90° (1).

$\bar{C}$  on oxidn. in s.t. at 200° with dil.  $HNO_3$  ( $D = 1.15$ ) yields (1) phthalic ac. (1:0820), converted in m.p. tube to phthalic anhydride (1:0725), m.p. 128° (1).

$\bar{C}$  on oxidn. with  $CrO_3$  in AcOH or dil.  $H_2SO_4$  gives (although in poor yield (1)) 2,3-dichloronaphthoquinone-1,4 (3:4857), gold-yel. ndls. (from alc.), m.p. 190°.

3:2935 (1) Claus, Knorr, *Ber.* 18, 2926-2929 (1885).



## 3:2905 8-CHLORONAPHTHOL-2

 $C_{10}H_7OCl$ 
 Beil. VI - 640  
 VI<sub>1</sub>—  
 VI<sub>2</sub>-(604)

 M.P. 101° u.c. (1) B.P. 307-308° (1)  
 101° (2) (3) (5)

Ndls. from lgr.; very eas. sol. alc., ether, AcOH;  $C_2H_5$ ,  $CHCl_3$ ; spar. sol. pet. ether. — Volatile with steam. —  $\bar{C}$  depresses m.p. of 6-chloronaphthol-2 (3:3500) to 79-88° (5).

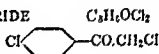
[For prepn. of  $\bar{C}$  from sodium 2-hydroxynaphthalenesulfonate-8 (Beil. XI-286, XI<sub>1</sub>-(67)) with 2 moles  $PCl_5$  at 150-160° see (1) (note that some 1,7-(2,8)dichloronaphthalene (3:1355) is also formed and that its proportion increases with more  $PCl_5$  or at higher temp. (1)); from 8-aminonaphthol-2 (Beil. XIII-685) via diazotization and use of  $Cu_2Cl_2$  reactn. see (2); for formn. of  $\bar{C}$  (20% yield (3)) from  $\beta$ -naphthol (1:1540) by treatment with soln. of  $Na_2CO_3 + Cl_2$  see (3) (note that 30% of 2,2'-dihydroxybinaphthyl-1,1' (Beil. VI-1051, VI<sub>1</sub>-(519)) together with n tar is also formed (3)).]

[ $\bar{C}$  (2 pts.) with benzaldehyde (1 pt.) with 7 pts.  $HBr/AcOH$  soln. stood for 24 hrs. gives (75% yield (2)) *meta*-phenyl-dichlorodibenzoxanthane, colorless ndls. from acetone, m.p. 213-214.5° (2).]

[ $\bar{C}$  (as sodium salt) treated with  $CO_2$  under press. at elevated temp. as directed gives (4) 8-chloro-2-hydroxynaphthoic acid-3, pale yel. ndls. from hot  $C_2H_5$ , m.p. 250° (4).]

$\bar{C}$  8-Chloro-2-naphthyl *m*-nitrobenzoate: citron-yel. ndls. from hot  $C_2H_5$  on addn. of 4 vols. hot alc., m.p. 176° (5). [From  $\bar{C}$  in warm dil. aq.  $NaOH$  on shaking with *m*-nitrobenzoyl chloride (5).]

3:2965 (1) Claus, Volz, *Ber.* 18, 3157-3158 (1885). (2) Dillthey, Quint, Helsen, *J. prakt. Chem.* (2) 152, 72-75 (1939)  
 II 767; *C.A.* 22, 339  
*Cent.* 1933, II 446.

 3:2990  $\beta$ -CHLOROPHENACYL CHLORIDE  
 (Chloromethyl *p*-chlorophenyl  
 ketone)
 $C_8H_7OCl_2$ 
 Beil. VII - 282  
 VII<sub>1</sub>-(152)

 M.P. 101-102° (2) B.P. 270° (1)  
 101° (1)

Ndls. (from alc.).

[For prepn. from *p*-chloroacetophenone (3:6735) by chlorination in  $CS_2$  see (1); from chloroacetyl chloride (3:5235) + chlorobenzene (3:7903) +  $CS_2 + AlCl_3$  see (2).]

$\bar{C}$  on oxidn. with alk.  $KMnO_4$  yields *p*-chlorobenzoic ac. (3:4340).

$\bar{C}$  on treatment with  $Br_2$  gives (3)  $\omega$ -bromo-*p*- $\alpha$ -dichloroacetophenone, cryst. from alc., m.p. 83-83.5° (3). —  $\bar{C}$  with  $KCN$  yields (4) *p*-chlorobenzoylacetonitrile, m.p. 129.5-130° (4). —  $\bar{C}$  with  $KSCN$  yields (4) *p*-chlorophenacyl thiocyanate, m.p. 138.6-139.2° (4). —  $\bar{C}$  with  $Na_2S$  at 60° gives (5) bis-(*p*-chlorophenacyl) sulfide, m.p. 121-121.6° (5).

$\bar{C}$  in  $MeOH$  treated with  $NH_2OH \cdot HCl$  yields (6) corresponding oxime, chloromethyl *p*-chlorophenyl ketoxime, m.p. 100.5-101° (6). [Note that although this deriv. has m.p. too similar to that of original  $\bar{C}$  to be used as identification itself, upon htg. at 100° with conc.  $H_2SO_4$  and pouring into aq. it is converted by Beckmann rearr. to chloroaceto-*p*-chloroanilide (Beil. XII-612), m.p. 168° (6), ndls. from alc., m.p. 169° (7).]

$\bar{C}$  (1 mole) in alc. gradually added to phenylhydrazine (2 moles) in alc. with cooling ppts. (8) 1-phenyl-3-chlorophenyl- $\Delta^2$ -diazene-1,2, yel ndls. from alc., m.p. 164-164.5° (8).

3:2990 (1) Gautier, *Ann. chim.* (6) **14**, 395-396 (1888). (2) Collet, *Compt. rend.* **125**, 718 (1897). (3) Rabcewicz-Zubkowski, *Roczniki Chem.* **9**, 532-537 (1929); *C.A.* **24**, 92 (1930). (4) Rabcewicz-Zubkowski, Kałinska, *Roczniki Chem.* **10**, 541-569 (1930); *C.A.* **25**, 505 (1931). (5) Chrzaszczewska, Chwalinski, *Roczniki Chem.* **7**, 67-73 (1927); *Cent.* **1927**, 11 415; *C.A.* **22**, 1339 (1928). (6) Collet, *Bull. soc. chim.* (3) **27**, 510 (1902). (7) Beckurts, Frerichs, *Arch. Pharm.* **253**, 241 (1915). (8) Bodforss, *Ber.* **52**, 1762, 1772-1773 (1919).

# CHAPTER VIII

## DIVISION. A. SOLIDS

(3:3000-3:3499)

3:3005 5,6-DICHLORO-3,4-DIMETHYLPHENOL  
(5,6-Dichloro-*o*-4-xylenol)



$C_6H_3OCl_2$

Beil. S.N. 529

M.P. 102.5° (1)  
102° (2)

Cryst. from lt. pet. — Very sol. most organic solvents. — Volatile with steam.

[For prepn. of  $\bar{C}$  from 5,6-dichloro-3,4-dimethylaniline (5,6-dichloro-*o*-4-xylidine) (3) via diazotization and hydrolysis (yield not stated) see (1); for formn. of  $\bar{C}$  from 4,5,6-trichloro-1,1-dimethylcyclohexen-4-one-3 with conc.  $H_2SO_4$  at 110–120° (yield not stated) see (2).]

$\bar{C}$  with  $Cl_2$  in lt. pet. readily gives (2) 2,5,6-trichloro-3,4-dimethylphenol (3:4747), m.p. 182°.

The nitration of  $\bar{C}$  has not been reported, and the expected 2-nitro-5,6-dichloro-3,4-dimethylphenol is unknown.

— 5,6-Dichloro-3,4-dimethylphenyl acetate: unreported.

Ⓔ 5,6-Dichloro-3,4-dimethylphenyl benzoate: m.p. 97.5° (1), 94° (2).

3:3005 (1) Hinkel, Ayling, Bevan, *J. Chem. Soc.* 1928, 2532–2533. (2) Hinkel, *J. Chem. Soc.* 125, 1851 (1924). (3) Hinkel, Ayling, Bevan, *J. Chem. Soc.* 1928, 1877.

3:3015 1,3,5-TRICHLORONAPHTHALENE



$C_{10}H_5Cl_3$

Beil. V - 545

V<sub>1</sub>-(263)

V<sub>2</sub>-(446)

M.P. 103° (1) (2) (4)  
102–103° (3)  
94° (8)

[For prepn. of  $\bar{C}$  from 1,3-dichloronaphthalenesulfonyl chloride-5 [Beil. XI-163] (4) (5), from 1,5-dichloronaphthalenesulfonyl chloride-3 [Beil. XI-182] (1), from 1-chloro-5-nitronaphthalenesulfonyl chloride-3 [Beil. XI-182] (5), or from 1-chloronaphthalene-3,5-bis(sulfonyl chloride) [Beil. XI-215] (7), each with  $PCl_5$  as directed, see indic. refs.; from 1,7-dichloronaphthylamine-3 (8) via diazotization and use of  $Cu_2Cl_2$  reactn. see (8); for formn. of  $\bar{C}$  (together with other products) from 1-nitronaphthalene [Beil. V-553, V<sub>1</sub>-(264)] with  $Cl_2$  (2) in pres. of  $I_2$  +  $FeCl_3$  (3) see indie. refs.]

[ $\bar{C}$  treated with  $ClSO_3H$  in  $CS_2$  and reactn. prod. conv. to K salt as directed (1) yields potassium 1,3,5-trichloronaphthalenesulfonate-7 (corresp. sulfonyl chloride, m.p. 152° (1)).]

3:3015 (1) Turner, Wynne, *J. Chem. Soc.* 1941, 247, 253. (2) Atterberg, *Ber.* 9, 317 (1878). (3) Buffle, Corbaz, *Arch. sci. phys. nat.* 14, 149-153 (1932); *Cent.* 1932, II 3394. (4) Widman, *Ber.* 12, 2230 (1879). (5) Armstrong, Wynne, *Chem. News* 61, 274 (1890). (6) Cleve, *Chem. Ztg.* 17, 758 (1893). (7) Armstrong, Wynne, *Chem. News* 62, 162 (1890). (8) Friedländer, Karamessinis, Schenk, *Ber.* 55, 48-49 (1922).

## 3:3045 4-CHLORONAPHTHOL-2

 $C_{10}H_7OCl$ 

Beil. S.N. 538

M.P. 104° (1)  
103-104° (2)  
102-103° (2)  
100° (4)

Ndls. from lgr. or 30% aq. alc.

[For prepn of  $\bar{C}$  from 1,4-dichloronaphthol-2 (3:3840) by partial reduction with  $SnCl_2$  in  $AcOH/HCl$  at 100° in a.t. for 8 hrs (74% yield (2)) (1) see indic. refs., from 4-chloronaphthol-2-sulfonic acid-1 (2) (see also under 3:3840) by hydrolysis of the sulfonic acid group (91% yield) see (2); from 4-chloronaphthalene-1,2-diazo-oxide (itself obtd. in 95% yield (3) from 4-chloro-2-nitronaphthylamine-1 with  $HNO_2$ ) on boilg. with  $Al$  powder in  $EtOH$  for 19 hrs. (84% yield (4)) or (less advantageously) with  $Na_2SnO_2$  (4) see indic. refs.]

$Na\bar{A}$  is spar. sol. in cold aq 10%  $NaOH$  (4).

[ $\bar{C}$  with alc.  $NaOH + CHCl_3$  (3:5050) undergoes Reimer-Tiemann reaction giving (but in very small yield (2)) 4-chloro-2-hydroxynaphthaldehyde-1, m.p. 118° (2).]

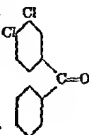
$\bar{C}$  (in alk. soln.) with diazotized aniline gives (4) 4-chloro-1-benzeneazonnaphthol-2, or-red ndls. from acetone, or crimson ndls. from chlorobenzene, m.p. 165° (4) (note that after fusion and resolidification this prod. has m.p. 151° but after a second resolidification (at about 155°) remelts on slow htg. at 165° (4)). [For use of  $\bar{C}$  in prepn. of azo dyes by coupling with o-hydroxydiazonium salts see (5).]

— 4-Chloro-2-naphthyl methyl ether: pl. from lt. petroleum, m.p. 44-45° (4). [From  $\bar{C}$  with  $Me_2SO_4 + aq. NaOH$  (3)]

⊙ 4-Chloro-2-naphthyl acetate: pl. from aq.  $MeOH$  or lt. petroleum, m.p. 58-59° (2), 56° (4) [From  $\bar{C}$  with excess  $Ac_2O$  refluxed 30 min. (90-100% yield (2)).]

⊙ 4-Chloro-2-naphthyl benzoate: ndls. from alc., m.p. 83-84° (2).

3:3045 (1) Fries, Schimmelschmidt, *Ann.* 484, 293 (1930). (2) Burton, *J. Chem. Soc.* 1945, 280-283. (3) Hodgson, Birtwell, *J. Chem. Soc.* 1943, 322. (4) Hodgson, Birtwell, *J. Chem. Soc.* 1943, 463-469. (5) Herzberg, Wunderlich (to I.G.), *Ger.* 459,889, May 18, 1928; *Cent.* 1928, II 395; not in *C.A.*

3:3070 3,4-DICHLOROBENZOPHENONE  
(3,4-Dichlorophenyl phenyl ketone) $C_{13}H_9OCl_2$  Beil. S.N. 652

M.P. 104-105° (1)  
102-103° (2) (3)

Cryst. (from alc. (1)).

[For prepn. (79.5% yield) from *o*-dichlorobenzene (3:6055) + BzOH (1:0715) + AlCl<sub>3</sub> see (1); for prepn. from *o*-dichlorobenzene (3:6055) + BzCl (3:6240) + AlCl<sub>3</sub> see (2) (3).]

⑥ 3,4-Dichlorobenzophenone oxime: m.p. 153–154° (1). [This oxime upon Beckmann rearr. with H<sub>2</sub>SO<sub>4</sub> gives (1) 3,4-dichlorobenzanilide which can be hydrolyzed to 3,4-dichlorobenzoic ac. (3:4925), m.p. 207–208° (1), and aniline]

3:3070 (1) Newton, Groggins, *Ind. Eng. Chem.* 27, 1398 (1935). (2) Böeseken, *Rec.* 27, 15 (1905). (3) Kraay, *Rec. trav. chim.* 49, 1085 (1930).

### 3:3100 4-CHLORORESORCINOL



C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>Cl

Beil. VI —

VI<sub>1</sub>—

VI<sub>2</sub>-(818)

M.P. 105° (1) (10)

102° (2)

B.P. 259.5° (2)

255–256° (4)

147° at 18 mm. (1)

The nature of the cpd., m.p. 89°, and formerly (3) thought to be  $\bar{C}$ , is still in doubt, cf. (1).  $\bar{C}$  is very sol. in nq. and *not* volatile with steam (1); eas. sol. aq., alc., ether, C<sub>6</sub>H<sub>6</sub>, and CS<sub>2</sub> (4).

[For prepn. of  $\bar{C}$  from resorcinol (1:1530) by actn. of SO<sub>2</sub>Cl<sub>2</sub> in ether (95% yield (1)) see (1) (4).]

$\bar{C}$  with FeCl<sub>3</sub> gives a blue-violet soln. becoming brown on warming (4).

$\bar{C}$  reduces NH<sub>4</sub>OH/AgNO<sub>3</sub> on warming (4).

$\bar{C}$  on further chlorination with SO<sub>2</sub>Cl<sub>2</sub> (no details) gives (96% yield (1)) of 4,6-dichlororesorcinol (3:3380).

$\bar{C}$  (10 g.) refluxed with KHCO<sub>3</sub> (40 g.) in nq. (50 ml.) for 1½ hrs. gives (76% yield (5)) of 5-chloro-2,4-dihydroxybenzoic acid (6), cryst. from hot aq., m.p. 224–225° cor. (6), 215–216° (Maquenne bloc) after drying at 100–105° (5) (6).

$\bar{C}$  in AcOH treated with xanthrol (1:5205) yields 4-chloro-2-(?)-xanthidylresorcinol, cryst. from C<sub>6</sub>H<sub>6</sub>, m.p. 215° (7).

[For studies on prepn. of alkyl ethers of 4-chlororesorcinol for use as antiseptics and germicides see (8); for use of  $\bar{C}$  in prepn. of purpurin (1,2,4-trihydroxyanthraquinone) by reaction with phthalic anhydride, H<sub>2</sub>SO<sub>4</sub> + H<sub>3</sub>BO<sub>3</sub>, see (9) ]

[For coupling of  $\bar{C}$  with diazotized aniline, *p*-nitroaniline, or *p*-toluidine see (11).]

⑥ 4-Chlororesorcinol diacetate: m.p. 46–47° (10).

⑥ 4-Chlororesorcinol dihenzoate: m.p. 66° (10).

3:3100 (1) Moore, Day, Suter, *J.*

*J. Gen. Chem. (U.S.S.R.)* 3, 164–171

*J. Am. Chem. Soc.* 55, 319–320 (1933).

(5) Fabre, *Ann. chim.* (9) 18, 79–81 (1922). (6) Sandin, McKee, *J. Am. Chem. Soc.* 57, 1011–1078 (1935). (7) Ref. 5, pp. 108–109. (8) Read (to Lambert Pharmacal Co.), U.S. 2,036,827, April 7, 1936; *Cent.* 1937, I 697; *C.A.* 30, 3592 (1936). (9) Lee, Buxbaum (to du Pont Co.), U.S. 1,985,452, Dec. 25, 1934; *Cent.* 1935, II 439; *C.A.* 29, 1104 (1935). (10) Petyunin, *J. Gen. Chem. (U.S.S.R.)* 14, 203–210 (1944); *C.A.* 39, 2285 (1945).

(11) Petyunin, *J. Gen. Chem. (U.S.S.R.)* 14, 303–311 (1944); *C.A.* 39, 4060 (1945).

## 3:3130 2-CHLOROHYDROQUINONE



Beil. VI - 849

VI<sub>1</sub>-(417)VI<sub>2</sub>-(844)

M.P. 106°	(1) (2) (12)	B.P. 263°	(1) (2)
105.5° cor.	(3)		
104°	(4) (5)		
103°	(6)		
102°	(7)		
101-102°	(8)		

[See also 2-chlorobenzoquinone-1,4 (3:1100).]

Colorless lfts from  $\text{CHCl}_3$  in which  $\bar{\text{C}}$  is eas. sol. hot but spar. sol. cold. — Very eas. sol. aq., alc., or ether; sol. in warm  $\text{C}_6\text{H}_6$  (dif. from hydroquinone (1:1590) and use in sepn. from latter (1)). — Not sublimable (5)

[For prepn. of  $\bar{\text{C}}$  from 2-chlorobenzoquinone-1,4 (3:1100) by reductn. with aq.  $\text{SO}_2$  (2) (9) see indic. refs. (note, however, that in dil. aq.  $\text{NaOH}$  under  $\text{N}_2$  both reductn. and sulfonation occur (10)); from benzoquinone-1,4 (1:9025) with conc.  $\text{HCl}$  (11) (2) or in  $\text{CHCl}_3$  with  $\text{HCl}$  gas (100% yield (12)) (2); from sodium benzoquinonesulfonate (5) with conc.  $\text{HCl}$  below 20° (55% yield (5)) in  $\text{CO}_2$  see indic. refs.; from *p*-benzoquinone dichloride (2,3-dichlorocyclohexen-5-dione-1,4) [Beil. VII-573] by reductn. with  $\text{SnCl}_2 + \text{HCl}$  at 0° see (4); from hydroquinone (1:1590) in  $\text{CCl}_4$  with  $\text{Cl}_2$  see (13).]

[ $\bar{\text{C}}$  is used as a photographic developer under name "Adurol" (for identification of  $\bar{\text{C}}$  in developers see (1));  $\bar{\text{C}}$  forms an addn. cpd. (14) with 2 moles *p*-(methylamino)phenol also used as developer under name Chloranol; for use of  $\bar{\text{C}}$  as vulcanization accelerator see (15); for use of  $\bar{\text{C}}$  as antioxidant (16) and as gum inhibitor in cracked gasoline (17) or in aq. emulsion as insecticidal spray (18) see indic. refs.; for study of bactericidal actn. see (19).]

$\bar{\text{C}}$  on oxidn. with  $\text{NaClO}_3 + \text{H}_2\text{SO}_4 + \text{V}_2\text{O}_5$  in  $\text{AcOH}$  (92% yield (20)), with  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$  (yield: 89% (21), 84% (8)) (2), with  $\text{MnO}_2 + \text{dil. H}_2\text{SO}_4$  (56% yield (8)), or with  $\text{PbO}_2$  in  $\text{C}_6\text{H}_6$  (22) gives 2-chlorobenzoquinone-1,4 (3:1100). [For studies of oxidn.-reductn. potential of this system and also for the intermediate quinhydrone see under the quinone (3:1100).]

[For reactn. of  $\bar{\text{C}}$  with phthalic anhydride + conc.  $\text{H}_2\text{SO}_4$  at 130-135° see (2); for reactn. of  $\bar{\text{C}}$  with naphthalene-1,2-dicarboxylic acid anhydride (23) or with naphthalene-2,3-dicarboxylic acid anhydride (24) each fused with  $\text{AlCl}_3 + \text{NaCl}$  see indic. refs.]

$\bar{\text{C}}$  in  $\text{AcOH}$  with xanthinol (1:5205) yields (25) 2-chloro-3-xanthidrylhydroquinone, cryst. from  $\text{C}_6\text{H}_6$ , m p 236-237° (25).

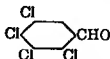
$\bar{\text{C}}$  gives no effervescence with aq. 10%  $\text{Na}_2\text{CO}_3$  but soln. darkens on stdg. (1);  $\bar{\text{C}}$  with aq. 5%  $\text{AgNO}_3$  scarcely reduces in cold but does so rapidly on warming (1);  $\bar{\text{C}}$  with 10% aq.  $\text{FeCl}_3$  gives red-brown color in cold and on boilg. pronounced quinone-like odor (1).

① 2-Chlorohydroquinone diacetate: pr. from dil. alc., m p. 99° (1) (26), 72° (2), 71-72° (27), 70.5° cor. (3) [from  $\bar{\text{C}}$  with  $\text{Ac}_2\text{O}$  (2) or  $\text{AcCl}$  (26)] [Note that a monoacetate, m p. 62° (28) has been reported, but the reason for the wide divergence in the m p.'s reported for the diacetate has not been explained.]

② 2-Chlorohydroquinone dibenzoate: fine woolly ndls. from mixt. of alc. + ether, m p. 130° (2). [From  $\bar{\text{C}}$  on refluxing with  $\text{BzCl}$  (2)]

*Chem. Soc.* 1934, 680. (17) Betts, Hammett, *J. Am. Chem. Soc.* 59, 1568-1572 (1937). (18) Kindler, *Ann.* 452, 108 (1927). (19) Mehner, *J. prakt. Chem.* (2) 62, 560-565 (1900). (20) Menon, *J. Chem. Soc.* 1936, 1775-1777. (21) Jenkins, *J. Am. Chem. Soc.* 55, 2898 (1933). (22) Ivanov, *Bull. soc. chim.* (5) 4, 686 (1937).

**3:3140 2,3,4,5-TETRACHLORO-BENZALDEHYDE**



$C_7H_2OCl_4$  Beil. S.N. 635

M.P. 106-106.5° (1)

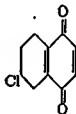
[For prepn. of  $\bar{C}$  from 2,3,4,5-tetrachlorobenzal (di)chloride (3:9397) by hydrolysis (presumably with strong  $H_2SO_4$ ) see (1).]

$\bar{C}$  with  $NaHSO_3$  forms the corresp. addn. cpd. which may be used as means of sepn. of  $\bar{C}$  from 2,3,5,6-tetrachlorobenzaldehyde (3:2700).

[For use of  $\bar{C}$  in prepn. of dyestuffs see (1).]

**3:3140** (1) Chem. Fabrik Griesheim-Elektron, Brit. 251,511, May 27, 1926; *Cent.* 1926, II 2355; [*C.A.* 21, 1361 (1927)]; French 603,650, April 20, 1926; *Cent.* 1926, II 2355; not in *C.A.*

**3:3145 6-CHLORONAPHTHO-QUINONE-1,4**



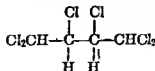
$C_{10}H_6O_2Cl$  Beil. S.N. 674

M.P. 106-107° (1)

[For prepn. of  $\bar{C}$  from benzoquinone-1,4 (1:9025) by addition of 2-chlorobutadiene-1,3 ("Chloroprene") (3:7080) and subsequent oxidation of the resulting Diels-Alder type adduct see (2); for formn. of  $\bar{C}$  by oxidation of various dichloronaphthalenes see (1).]

**3:3145** (1) Kozlov, Talybov, *J. Gen. Chem.* 9, 1827-1836 (1939); *C.A.* 34, 4067 (1940). (2) Carothers, Collins (to du Pont Co.), U.S. 1,967,862, July 24, 1934; *Cent.* 1936, I 2209; *C.A.* 28, 5994-5995 (1934).

**3:3155 1,1,2,3,4,4-HEXACHLORO-BUTANE**



$C_4H_2Cl_6$  Beil. S.N. 10

M.P. 107° (1) (2)

[For isolation of  $\bar{C}$  from the high-boilg. fraction resulting in the preparation of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1) (2); long refluxing (20 days) of freshly distilled samples of the latter compound also yields (1)  $\bar{C}$ .]

$\bar{C}$  on boilg. with alc.  $Ca(OH)_2$  or with alk. at room temp. loses 2 HCl yielding (1) the liquid stereoisomer (3:6150) of 1,2,3,4-tetrachlorobutadiene-1,3. [The solid stereoisomer (3:0870) was not obtained from  $\bar{C}$  (1).]

**3:3155** (1) Müller, Hüther, *Ber.* 64, 589-600 (1931); *C.A.* 25, 3956-3957 (1931). (2) Ghigli, *Ann. chim. applicata* 28, 363-368 (1938); *Cent.* 1939, I 86; *C.A.* 33, 6792 (1939).





nitronaphthalene [Beil. V-553, V<sub>1</sub>-(264)] with Cl<sub>2</sub> (together with other products) (17) (2) see indic. refs.]

[C̄ in CHCl<sub>3</sub> soln. satd. with Cl<sub>2</sub> gives (25) both 1,5-dichloronaphthalene tetrachloride, m.p. 84°, and a trichloronaphthalene dichloride, m.p. 94° (separated by spar. soly. of latter in MeOH).]

[C̄ on mononitration yields (10) 1,5-dichloro-8-nitronaphthalene [Beil. V-556], yel. pr. from AcOH, m.p. 142° (10) (17) (23); note that the isomeric 1,5-dichloro-3-nitronaphthalene, m.p. 132°, has been reported indirectly (23) (12).]

[C̄ on monosulfonation (18) (13) gives chiefly 1,5-dichloronaphthalenesulfonic acid-3 [Beil. XI-183, XI<sub>1</sub>-(41)] (corresp. sulfonyl chloride, m.p. 143° (13), corresp. sulfonamide, m.p. 204° (24)) accompanied by a smaller amt. 1,5-dichloronaphthalenesulfonic acid-2 [Beil. XI-181] (corresp. sulfonyl chloride, m.p. 125° (13)).]

[C̄ with picric acid yields a cpd. C̄.PkOH, m.p. 87° (10).]

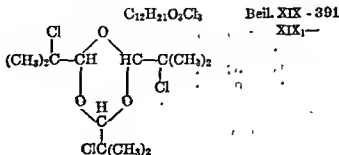
[C̄ on oxidn. with CrO<sub>3</sub>/AcOH yields (19) 3-chlorophthalic acid (3:4820) but on oxidn. with dil. HNO<sub>3</sub> yields (20) a nitro-chloro-phthalic acid.] [C̄ on cat. vapor-phase oxidn. (21) gives 80% yield 3-chlorophthalic anhydride (3:3900) + 20% phthalic anhydride (1:0725).]

3:3200 (1) Erdmann, *Ann.* 247, 353-354 (1888). (2) Weissberger, Sängewald, Hampeon, *Trans. Faraday Soc.* 30, 890 (1934). (3) Krollpfeiffer, *Ann.* 430, 198 (1923). (4) Beattie, Whitmore, *J. Am. Chem. Soc.* 55, 1546-1548 (1933). (5) Ferrero, Bolliger, *Helv. Chim. Acta* 11, 1146-1147 (1928). (6) Armstrong, Wynne, *Proc. Chem. Soc.* 1930, 81. (7) Armstrong, Wynne, *Chem. News* 61, 274 (1890). (8) Armstrong, Wynne, *Proc. Chem. Soc.* 1930, 81. (9) Cleve, *Bull. soc. chim.* (2) 26, 540 (1876).

(11) Erdmann, *Ber.* 20, 3185-3186 (1887). (12) Kalle and Co., *Ger.* 343,147, Oct. 28, 1921; *Cent.* 1922, II 143. (13) Turner, Wynne, *J. Chem. Soc.* 1941, 253. (14) Cleve, *Chem. Ztg.* 17, 398 (1893). (15) Armstrong, Wynne, *Chem. News* 76, 69-70 (1897). (16) B.A.S.F., *Ger.* 234,912, May 26, 1911; *Cent.* 1911, II 63. (17) Atterberg, *Ber.* 0, 316-318, 926-928 (1877). (18) Armstrong, Wynne, *Proc. Chem. Soc.* 1890, 81. (19) Guareschi, *Gazz. chim. ital.* 17, 120 (1887). (20) Atterberg, *Ber.* 10, 547-548 (1877).

(21) Pongratz, Bassi, Fuchs, Süss, Wüstner, Schober, *Angew. Chem.* 54, 22-25 (1941). (22) Röchling'sche Eisen und Stahlwerke, *Ger.* 415,228, June 16, 1925; *Cent.* 1925, II 1239. (23) Friedländer, Karamessinis, Schenk, *Ber.* 55, 47-50 (1922). (24) Armstrong, Wynne, *Chem. News* 61, 274 (1890). (25) Wynne, *J. Chem. Soc.* 1946, 61.

3:3220 PARA- $\alpha$ -CHLORO-ISOBUTYRALDEHYDE  
(2,4,6-tris-( $\alpha$ -Chloroisopropyl)-trioxane-1,3,5)



M.P. 107° (1) (2)

Odorless tasteless ndls. (from distn. with steam); pr. (from ether); insol. aq.; sol. alc., ether, pet. ether. — Sublimes above m.p.

[For prepn. from  $\alpha$ -chloroisobutyraldehyde (3:7235) by shaking with 1/2 vol. conc. H<sub>2</sub>SO<sub>4</sub> see (1) (2).]

3:3220 (1) Brochet, *Ann. chim.* (7) 10, 357-359 (1897). (2) Brochet, *Bull. soc. chim.* (3) 7, 643-644 (1892).

## 3:3250 2,4-DICHLORONAPHTHOL-1

 $C_{10}H_6OCl_2$ 

Beil. VI - 612

VI<sub>1</sub>-(308)VI<sub>2</sub>-(582)

M.P. 107-108° (2) (3)

106-107° (1) (5)

Ndls. (from dil. alc. or lgr.); from AcOH  $\bar{C}$  separates in pr. with 1 mole of AcOH rapidly lost at 40-50° (1). —  $\bar{C}$  is volatile with steam; eas. sol. nbs. alc. ether or  $C_6H_6$ . —  $\bar{C}$  on htg. to 180° decomposes with loss of HCl.

[For prepn. from  $\beta$ -naphthol (1:1500) (1) (2) or 4-chloronaphthol-1 (3:3720) (4) by chlorination see (1) (2) (3); from naphthalene 1,2,3,4-tetrachloride (3:4750) by oxidn. with  $CrO_2$  in AcOH see (5); for other methods see Beil. VI-612]

$\bar{C}$  dissolves in NaOH or  $Na_2CO_3$  but on warming (or even long stdg. in cold) yields (6) ultramarine flocks which impart to ether a violet, and to benzene a deep blue violet, color (6). [Same result obtd. with  $K_3Fe(CN)_6$  but not with pyridine (6).]

$\bar{C}$  on bofl. with dil.  $HNO_3$  is oxidized (1) to phthalic ac. (1:0820); but with  $CrO_2$  in AcOH yields 2-chloronaphthoquinone-1,4 (3:3580), volatile with steam, golden-yel. ndls. from aq., alc., or AcOH, m.p. 116° (1).

$\bar{C}$  is not affected by Sn + alc. HCl (3), or Na/Hg (3), but on htg. in AcOH with conc. HI ( $D = 1.7$ ) for 10 hrs. gives (3)  $\alpha$ -naphthol (1:1500).

$\bar{C}$  dislvd. in 20 pts. 15% aq. KOH and shaken with 4 pts.  $(CH_3)_2SO_4$  gives (94% yield (3)) of the methyl ether, methyl 2,4-dichloro-1-naphthyl ether, colorless ndls. from alc., m.p. 58° (3).

② 2,4-Dichloro-1-naphthyl acetate: from  $\bar{C}$  by htg. with AcCl (2); ndls. (from alc.), m.p. 74-76° (2).

3:3250 (1) Cleve, *Ber.* 21, 891-893 (1885) (2) Zincke, *Ber.* 21, 1035-1036 (1888). (3) Franzen, *Stübke, J. prakt. Chem.* (2) 103, 354-385 (1921/22). (4) Reverdin, Kauffmann, *Ber.* 28, 3053 (1895). (5) Helbig, *Ber.* 28, 506 (1895). (6) Willstätter, Schuler, *Ber.* 61, 370 (1928).

## 3:3275 6-CHLORO-2-METHYL-BENZOIC ACID

 $C_8H_7O_2Cl$ 

Beil. S.N. 941

M.P. 108° (1)

102° (2)

[91.5° (3)]

Long slender colorless ndls. from hot aq. (2) or from HCl (1).

[For prepn. of  $\bar{C}$  from 6-chloro-2-methylbenzamide (see below) (itself obtd. from 6-chloro-2-methylbenzonitrile, m.p. 82-83° (2)) by actn. of nitrous acid see (2); from 6-amino-2-methylbenzoic acid (1) via diazotization and use of  $Cu_2Cl_2$  reactn. see (1) (3).]

$\bar{C}$  on htg. with aniline,  $K_2CO_3$ , and copper powder yields (1) 3-methyldiphenylamine-carboxylic acid-2, cryst. from 50% alc., m.p. 145° dec. (1).

[ $\bar{C}$  melted and treated with  $Br_2$  evolves  $HBr$ , and the prod. on warming with dil. NaOH yields (3) 3-chloro- $\alpha$ -hydroxyphthalide, colorless pl. from dil. alc., m.p. 138° (3)]

— 6-Chloro-2-methylbenzamide: scales from boflg. aq., m.p. 167° (2). [Prepd. indirectly as above.]

3:3275 (1) Gleu, Nitzsche, *J. prakt. Chem.* (2) 153, 213 (1939). (2) Kenner, Witham, *J. Chem. Soc.* 119, 1458 (1921). (3) Levy, Stephen, *J. Chem. Soc.* 1930, 2788.

3:3295 3,4-DICHLORONAPHTHOL-2



$C_{10}H_8OCl_2$  Beil. VI —  
VI<sub>1</sub> —  
VI<sub>2</sub>-(004)

M.P. 108° (1) (2).

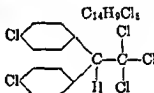
Small colorless ndls. from lgr. Sol. in cold  $K_2CO_3$  soln. (2).

[For prepn. from  $\beta$ -naphthol (1:1540) via 1-nitrosonaphthol-2, chlorination with  $SO_2Cl_2$  in tetrachloroethane to 1-nitroso-3,4-dichloronaphthol-2, reduction to 1-amino-3,4-dichloronaphthol-2 and thence via diazo reaction to  $\bar{C}$  see (1); for prepn. from 1,3,4-trichloronaphthol-2 by reduction with  $FeSO_4 + NaOH$  see (2).]

$\bar{C}$ . treated with 1 mole  $HNO_2$  yields 1-nitroso-3,4-dichloronaphthol-2, golden-yel. cryst. from AcOH, m.p. not given (1).

3:3295 (1) Marschall, *Bull. soc. chim.* (4) 43, 1367 (1928). (2) Herzberg, Spengler, Schmidt (to I.G.), Ger. 431,165, June 30, 1926; *Cent.* 1926, II 1196.

3:3298 1,1,1-TRICHLORO-2,2-bis-(p-CHLOROPHENYL)ETHANE  
("DDT", "p,p-DDT")



Beil. S.N. 479

M.P. 108.5-109 (20)

108-109° (1) cor. (27) (29)

108° (2) (28)

107-108° cor. (3)

107° (4)

106-107° (17)

105-106° (5)

105° (6)

[See also 1,1-dichloro-2,2-bis-(p-chlorophenyl)ethane, "DDD" (3:3320).]

Note that  $\bar{C}$  is the remarkable insecticide to which so much publicity is currently being given. Despite the general fanfare the amount of real scientific data which has been released at this writing is small, although very rapid publication is inevitable in the near future. No attempt can be made in this text to cover the utilization of  $\bar{C}$ , but attention is drawn to two bibliographies (7) (8) containing respectively 174 and 418 references, although most of these are to general and nontechnical reports. For an extensive review of chemistry of  $\bar{C}$  see (30).

[For patents on utilization of "DDT" as insecticide see (9) (10). — For studies of toxicology and pharmacology of "DDT" see (11) (12) (13) (14). — Note that  $\bar{C}$  is by rabbits in part excreted as di-(p-chlorophenyl)acetic acid (3:4612), m.p. 166-166.5° u.e. (24).]

Colorless cryst. from 95% alc. —  $\bar{C}$  is spar. sol. in 95% alc.; viz., 0.8 wt. % at 0°, 3.9 wt. % at 48° (3); spar. sol. pet. ether of b.p. 30-60° (3);  $\bar{C}$  is moderately sol. in  $CCl_4$ , ether, or  $CHCl_3$  (3); eas. sol. in pyridine, dioxane,  $C_6H_6$ , or acetone (3); for data and graph of wt. % solubility/temp. over range 0-48° see (3) cf. (25); for soly. of  $\bar{C}$  in kerosenes see (31). [For detn. of  $\bar{C}$  in technical samples, i.e., in pres. of "DDD" (3:3320), by recrystn. from satd. alc. soln. of "DDT" see (26).]

Note that technical  $\bar{C}$  may contain some of the isomeric 1,1,1-trichloro-2-(*p*-chlorophenyl)-2-(*o*-chlorophenyl)ethane (3:1820) and/or polymers of chloral (3:5210); in fact, technical  $\bar{C}$  of setting point  $88^\circ$  contains about 70%  $\bar{C}$  accompanied by 18% of the *o-p* isomer + 6% of the *o,o'* isomer (25). — For extensive report on the compn. of technical grade  $\bar{C}$  see (29).

[For optical crystallographic props. of  $\bar{C}$  see (28).]

### PREPARATION OF $\bar{C}$

$\bar{C}$  is universally prepd. by condensation of chloral or chloral hydrate with chlorobenzene.

From chloral hydrate. [For prepn. of  $\bar{C}$  from chloral hydrate (3:1270) with chlorobenzene (3:7903) + fuming  $H_2SO_4$  (8–10%  $SO_3$ ) (70% yield (2) (4)) or  $ClSO_3H$  (77% yield (32)) see indic. refs.]

From chloral. [For prepn. of  $\bar{C}$  from anhydrous chloral (3:5210) with chlorobenzene (3:7903) + conc.  $H_2SO_4$  see (6) (15) (16).]

### CHEMICAL BEHAVIOR OF $\bar{C}$

Reduction of  $\bar{C}$ .  $\bar{C}$  on reduction with  $Na/alc.$  gives up all its chlorine quant. detn. of which comprises a method for the quant. detn. of  $\bar{C}$  (14)

[ $\bar{C}$  on hydrogenation with  $H_2$  +  $Pd/CaCO_3$  in various solvents on slight warming gives according to conditions (18) various products of bimolecular reduction; these include 2,2,3,3-tetrachloro-1,1,4,4-tetra-(*p*-chlorophenyl)butane, cryst. from  $AcOEt$ , m.p.  $271.5^\circ$  (28% yield (18)), both higher-melting ( $229^\circ$ ) and lower-melting ( $174^\circ$ ) stereoisomers of 2,3-dichloro-1,1,4,4-tetra-(*p*-chlorophenyl)butene-2 (former 36% yield, latter in traces) (18), and perhaps other products; for much further study of these reaction products see the original references (18)]

[ $\bar{C}$  on electrolytic reduction in alc.  $HCl$  soln. gives (13% yield (10)) at the cathode 1,1,4,4-tetra-(*p*-chlorophenyl)butyne-2, pr. from  $AcOEt$ , m.p.  $174^\circ$  (19); note that this prod. on oxdn. with  $CrO_3/AcOH$  gives (91% yield (19)) 4,4'-dichlorobenzophenone (3:4270), m.p.  $145^\circ$ .]

Oxidation of  $\bar{C}$ . Attempts to oxidize  $\bar{C}$  with  $CrO_3/AcOH$  have given (5) no identifiable products.

Dehydrochlorination of  $\bar{C}$ .  $\bar{C}$  with alc. ions can be caused to split out 1  $HCl$  yielding 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (21) (for study of rate see (20))

$\bar{C}$  with alc. 10–20 min. (21) (for study of rate see (20)) gives (27) 81% (5) 1,1-dichloro-bis-(*p*-chlorophenyl)ethylene (3:2438) [for use of this reaction by detn. of ionized chlorine as means for detn. of  $\bar{C}$  in spray deposit see (21)]

$\bar{C}$  with excess  $Ba(OH)_2 \cdot 8H_2O$  in ethylene glycol refluxed 10–12 hrs. gives (33% yield (24)) di-(*p*-chlorophenyl)acetic acid (3:4612), m.p.  $166$ – $166.5^\circ$  u.c.; this results by initial loss of  $HCl$  as above and further degradation.

$\bar{C}$  in the pres. of minute amts. (e.g., 0.01%) of  $FeCl_3$  or  $AlCl_3$  at  $110$ – $120^\circ$  loses  $HCl$  giving (22) cf. (34) 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (3:2438). (See also below under behavior of  $\bar{C}$  with  $AlCl_3$  +  $C_6H_6$ .)

### SUBSTITUTION REACTIONS OF $\bar{C}$

Bromination. No study of the behavior of  $\bar{C}$  toward  $Br_2$  appears yet to have been reported.

Chlorination.  $\bar{C}$  in  $CCl_4$  soln. with  $Cl_2$  + trace of  $PCl_5$  in light at b.p. of mixture for 3 hrs. gives (73% yield (5)) 1,2,2,2-tetrachloro-1,1-bis-(*p*-chlorophenyl)ethane (3:2477), m.p.  $91$ – $92^\circ$  (5).

Nitration.  $\bar{C}$  on introduction of two nitro groups (no details) gives (6) n prod., ndls. from nlc., m.p. 148.0-148.3° (29), which is presumably 1,1,1-trichloro-1,2-bis-(4-chloro-2-nitrophenyl)ethane; note that this dinitro compd. has same m.p. as corresp. dinitro deriv. from "o,p-DDT" (3:1820) but m.p. of a mixt. of the two is depressed (29).

$\bar{C}$  on tetranitration with a mixt. (1:1 by volume) of fuming  $HNO_3$  and conc.  $H_2SO_4$  at 100° for 1 hr. gives (23) 1,1,1-trichloro-2,2-bis-(4-chloro-3,5-dinitrophenyl)ethane, m.p. 223.5-224.5° cor. (23). — [Note that similar tetranitration of "DDD" (1,1-dichloro-2,2-bis-(p-chlorophenyl)ethane (3:3320) gives (23) 1,1-dichloro-2,2-bis-(4-chloro-3,5-dinitrophenyl)ethane, m.p. 224.5-225.5° cor. (23); similar tetranitration of the o-p isomer of "DDT" (viz., 1,1,1-trichloro-2-(o-chlorophenyl)ethane) (3:1820) gives a prod., m.p. 229.5-230° cor. (23). — For color reactions of these tetranitro derivs. with MeOH/NaOMe and its use in detn. of  $\bar{C}$  see (23) (33).]

Behavior with  $AlCl_3 + C_6H_6$ .  $\bar{C}$  with anhydrous  $AlCl_3$  (1 mole) in large excess of  $C_6H_6$  reacts at room temp. evolving 2 moles HCl and giving (10%) yield (1) 1,1,2,2-tetraphenylethane [Beil. V-739,  $V_1$ -(371),  $V_2$ -(673)], m.p. 211°. [Note that the mechanism of this surprising result has not yet been explained; that by similar treatment the same tetraphenylethane is also obtd. in 25% yield from 1,1-dichloro-2,2-bis-(p-chlorophenyl)ethane (3:3320), in 10% yield from 1,1,1-trichloro-2,2-diphenylethane (3:1420), and from the o-p isomer of "DDT" (viz., 1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethane) (3:1820), but not at all from 1,1-dichloro-2,2-bis-(p-chlorophenyl)ethylene (3:2438); and that if chlorobenzene is substituted for  $C_6H_6$  no tetraphenylethane results from any of them (1).]

3:3298 (1) Fleck, Preston, Haller, *J. Am. Chem. Soc.* 67, 1419-1420 (1945). (2) Darling, *J. Chem. Education* 22, 170 (1945). (3) Gunther, *J. Am. Chem. Soc.* 67, 189-190 (1945). (4) Iris, *ibid.* 5, 71-74 (1944); *C.A.* 39, 495 (1945). (5) —150 (1945). (6) Zeidler, *Ber.* 7, 1181 and *Plant Quarantine*, 12 pp. (June 1945). (7) — pp. (May 1945). (8) 656 (1944). (10)

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328 (1942).

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## 3:3300 2,3,5-TRICHLORO-NAPHTHALENE

 $C_{10}H_5Cl_3$ 

Beil. V-540

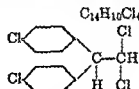
V<sub>1</sub>—  
V<sub>2</sub>—

M.P. 109.5° (1) (2)

[For prepn. of  $\bar{C}$  from 2,3-dichloronaphthol-8 (3:4315) (2) or from 2,3-dichloronaphthalenesulfonyl chloride-8 [Beil. XI-164] (1) (2) (3) with  $PCl_5$  see indic. refs.]

[ $\bar{C}$  treated with  $ClSO_3H$  in  $CS_2$  and reactn. prod. conv. to salts as directed (1) gives salts of 2,3,5-trichloronaphthalenesulfonic acid-8 (corresp. sulfonyl chloride, m.p. 164° (1)).]

3:3300 (1) Turner, Wynne, *J. Chem. Soc.* 1911, 247, 255-256. (2) Armstrong, Wynne, *Chem. News* 61, 275 (1890). (3) Armstrong, Wynne, *Proc. Chem. Soc.* 1890, 83; 1893, 79

3:3320 1,1-DICHLORO-2,2-bis-(p-CHLOROPHENYL)ETHANE  
("DDD"; "p,p'-DDD") $C_{14}H_{10}Cl_4$ 

Beil. S.N. 479

M.P. 109.5-110° (3)

109.4-110.2° cor. (5)

108.5-110° (4)

This compd. is closely related to "DDT" (3:3298) and occurs (4) as minor impurity in technical grades of this compound.

[For prepn. of  $\bar{C}$  from dichloroacetaldehyde (3:5180) or from 2,2-dichloro-1-(p-chlorophenyl)ethanol (4) with chlorobenzene (3:7903) + conc.  $H_2SO_4$  + fuming  $H_2SO_4$  (63% yield) see (4)]

$\bar{C}$  with alc. KOH refluxed 3 hrs. loses 1 HCl giving (77% yield (4)) (5) 1,1-dichloro-2,2-bis-(p-chlorophenyl)ethylene (3:1430).

$\bar{C}$  on dimnitration with 10 vols. fuming  $HNO_3$  at 50° for  $\frac{1}{2}$  hr. gives (90% yield (4)) a dinitro deriv.; cryst. from alc., m.p. 178-179° (4).

$\bar{C}$  on tetramitration with a mixt. (1:1 by volume) of fuming  $HNO_3$  + conc.  $H_2SO_4$  at 100° for 1 hr. gives (1) a prod., m.p. 224.5-225.5° cor., which presumably has the structure 1,1-dichloro-2,2-bis-(4-chloro-2,6-dinitrophenyl)ethane.

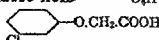
$\bar{C}$  with anhydrous  $AlCl_3$  (1 mole) + excess  $C_6H_6$  at ord. temp. evolves HCl and gives (25% yield (2)) 1,1,2,2-tetraphenylethane, m.p. 211° (2).

3:3320 (1) Schechter, Haller, *J. Am. Chem. Soc.* 66, 2129-2130 (1944). (2) Fleck, Preston, Haller, *J. Am. Chem. Soc.* 67, 1419-1420 (1945). (3) Cristol, Hayes, Haller, *Ind. Eng. Chem., Anal. Ed.* 17, 470-473 (1945). (4) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* 67, 1596, 1600 (1945). (5) Cristol, *J. Am. Chem. Soc.* 67, 1494-1498 (1945).

## 3:3325 m-CHLOROPHENOXYACETIC ACID

 $C_8H_7O_2Cl$ 

Beil. S.N. 522



M.P. 110° (1)

100.7-110.2° cor. (2)

Neut. Eq. 186.5

[For prepn. from m-chlorophenol (3:0255) by hgt. with chloroacetic ac. (3:1370) and aq. alk. see (1) (2)]

3:3325 (1) Koelsch, *J. Am. Chem. Soc.* 53, 304-305 (1931). (2) Hayes, Branch, *J. Am. Chem. Soc.* 65, 1555-1557 (1943)

3:3350 6-CHLORO-3-HYDROXY-  
BENZALDEHYDE  
(2-Chloro-5-hydroxy-  
benzaldehyde)

C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>ClBeil. VIII —  
VIII<sub>1</sub>-(526)

M.P. 111° (1)  
110.5-111.5° (2)

Colorless ndls. from dil. AcOH (1). — Very slowly volatile with steam (1). —  $\bar{C}$  has pronounced sternutatory propa. (1) (3).

[For prepn. from *m*-hydroxybenzaldehyde (1:0055) via direct chlorination see (2); via 4-nitro-3-hydroxybenzaldehyde, reductn. to corresp. amino cpd., and use of appropriate diazo reactn. see (1); for prepn. from *o*-chlorobenzaldehyde (3:6410) via nitration to 2-chloro-5-nitrobenzaldehyde, m.p. 78-79°, oximation, reduction to 2-chloro-5-aminobenzaldoxime, m.p. 159-160°, and finally diazotization and hydrolysis see (1); for prepn. from 4-chloro-3-methylphenol (3:1535) see (3); for prepn. from *p*-chlorophenol (3:0475) by condensation with chloral (3:5210) and subsequent alk. hydrolysis see (4).]

$\bar{C}$  in 50% AcOH mononitrated as specified (1) gives mixt. of 2-nitro and 4-nitro products eas. sepd. by volatility of latter with steam (1): 2-Nitro-6-chloro-3-hydroxybenzaldehyde: yel. ndls. from dil. AcOH, m.p. 136° (5), 138° (3). [Corresp. *p*-nitrophenylhydrazone, deep or.-red ndls. from AcOH, m.p. 256-257° dec. (5); semicarbazone, yel. ndls. from alc., m.p. 249-250° dec. (5).] 4-Nitro-6-chloro-3-hydroxybenzaldehyde: deep yel. ndls. from AcOH, m.p. 104° (5) (3). [Corresp. *p*-nitrophenylhydrazone, brick-red ndls. from AcOH, m.p. 284-286° dec. (5); semicarbazone, yel. pl. from alc., m.p. 266-267° dec. (5).]

$\bar{C}$  in aq. contg. NaHCO<sub>3</sub> treated (1) with Me<sub>2</sub>SO<sub>4</sub> yields 6-chloro-3-methoxybenzaldehyde, m.p. 62° (1). [Corresp. oxime, ndls., m.p. 101.5° (1); *p*-nitrophenylhydrazone, old-gold ndls., m.p. 229° (1).] [This methyl ether on oxidn. with KMnO<sub>4</sub> (1) yields 6-chloro-3-methoxybenzoic acid, ndls. from dil. AcOH, m.p. 170-171° (1).]

⑥ 6-Chloro-3-hydroxybenzaldoxime: colorless ndls. of monohydrate from dil. alc., from abs. alc. in anhydrous ndls., m.p. 146-147° (1).

— 6-Chloro-3-hydroxybenzaldehyde phenylhydrazone: unrecorded.

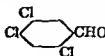
⑦ 6-Chloro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazone: red ndls. from dil. alc., m.p. 250-251° (1).

— 6-Chloro-3-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.

⑧ 6-Chloro-3-hydroxybenzaldehyde semicarbazone: pale yel. ndls., m.p. 236° (1).

3:3350 (1) Hodgson, Beard, *J. Chem. Soc.* 1926, 151-154. (2) Bissell, Kranz (to National Aniline and Chem. Co.), U.S. 1,776,803, Sept. 30, 1930; *Cent.* 1931, I 159; C.A. 24, 576S-576S (1930). (3) Friedländer, Schenck, *Ber.* 47, 3046-3047 (1914). (4) Haack, Smola, Austrian 141,159, March 25, 1935; *Cent.* 1935, II 439. (5) Hodgson, Beard, *J. Chem. Soc.* 1926, 2034.

3:3375 2,4,5-TRICHLOROBENZALDE-  
HYDE

C<sub>7</sub>H<sub>2</sub>OCl<sub>3</sub> Beil. VII-238  
VII<sub>1</sub>—

M.P. 112-113° (1)  
110-111° (2)

Colorless ndls. from conc. alc. soln. (1). — Insol. boilg. aq. but volatile with steam. — Eas. sol. alc., ether, C<sub>6</sub>H<sub>6</sub>, CHCl<sub>3</sub>, CS<sub>2</sub>.

[For prepn. of  $\bar{C}$  from 2,4,5-trichlorobenzal (di)chloride (3:6910) by hydrolysis with fuming  $H_2SO_4$  (1), with warm conc.  $H_2SO_4$  (3), or with aq. in s.t. at  $260^\circ$  (2) see indic. refs.]  
 $\bar{C}$  on oxidn. with  $KMnO_4$  should yield 2,4,5-trichlorobenzoic acid (3:4630), m.p.  $164^\circ$ , but this reaction is not actually reported in the literature; note that  $\bar{C}$  in air oxidizes only slowly (1).]

$\bar{C}$  with  $Na_2SO_3$  under press. gives (4) 5-chlorobenzaldehydesulfonic acid-2,4 [Beil. XI-325]

$\bar{C}$  with anhydrous  $NaOAc$  on htg. (Perkin synthesis) gives (1) 2,4,5-trichlorocinnamic acid, m.p.  $200-201^\circ$

[For use of  $\bar{C}$  in prepn. of dyestuffs see (5) (3)]

— 2,4,5-Trichlorobenzaldoxime: unreported.

— 2,4,5-Trichlorobenzaldehyde phenylthiohydrazone: unreported.

— 2,4,5-Trichlorobenzaldehyde *p*-nitrophenylthiohydrazone: unreported.

— 2,4,5-Trichlorobenzaldehyde 2,4-dinitrophenylthiohydrazone: unreported.

3:3375 (1) Seelig, *Ann.* 237, 147-149, 151 (1857). (2) Beilstein, Kuhlberg, *Ann.* 152, 235-239 (1869). (3) Fischer, *Ger.* 25,827, June 23, 1883, *Friedländer* 1, 42 (1877-87). (4) Geigy and Co., *Ger.* 193,909, June 1, 1908, *Cent.* 1908, II 214; [*C.A.* 2, 2733-2734 (1908)]. (5) Perkin, Clemo (to British Dyestuffs Corp.), *Brit.* 165,658, July 28, 1921, *C.A.* 16, 835 (1922).

### 3:3380 4,6-DICHLORORESORCINOL



$C_6H_4O_2Cl_2$

Beil. VI - 820

VI-(403)

VI-(819)

M.P.  $113.2^\circ$  (1) (2)

$112-113^\circ$  (3)

$108-109^\circ$  (4)

Cryst. from lgr. —  $\bar{C}$  is very sol. aq. (forms hydrate, m.p.  $70^\circ$ ) (1);  $\bar{C}$  is ex. sol. alc., ether (1). — [For bactericidal action of  $\bar{C}$  see (3).]

[For prepn. of  $\bar{C}$  from resorcinol (1:1530) with  $N,N'$ -dichlorourea see (1); from 4-chlororesorcinol (3:3100) with  $SO_2Cl_2$  (96% yield) see (3) cf. (4); (the prods. of m.p.  $77^\circ$ , b.p.  $249^\circ$  (5), and m.p.  $101^\circ$ , b.p.  $254^\circ$  (6), may have been impure samples of  $\bar{C}$ ).]

$\bar{C}$  with  $N,N'$ -dichlorourea +  $KBr$  gives (2) 2-bromo-4,6-dichlororesorcinol, m.p.  $101^\circ$ .

$\bar{C}$  with  $N,N'$ -dichlorourea +  $KI$  gives (7) 2-iodo-4,6-dichlororesorcinol, m.p.  $54^\circ$ .

$\bar{C}$  with ethyl  $\alpha$ -ethoxyacetoacetate in alc.  $NaOEt$  gives (4) 6,8-dichloro-2-ethoxycoumarin, m.p.  $235^\circ$ .

Note that  $\bar{C}$  does not (6) (9) condense with phthalic anhydride.

① 4,6-Dichlororesorcinol dimethyl ether: ndls. from alc., m.p.  $115^\circ$  (5),  $117-118^\circ$  (2)  $116-117^\circ$  (3). [From  $\bar{C}$  with  $Me_2SO_4$  + aq. alk. (3) (9).]

3:3380 (1) Likhoshesterov, *J. Gen. Chem. (U.S.S.R.)* 3, 164-171 (1932); *Chem. Zvest.* 1932, 1 157; *C.A.* 23, 1675 (1934). (2) Likhoshesterov, *J. Gen. Chem. (U.S.S.R.)* 3, 172-173; *Chem. Zvest.* 1932, 1 158; *C.A.* 23, 1676 (1934). (3) Likhoshesterov, *J. Am. Chem. Soc.* 54, 215-216 (1932); *Chem. Zvest.* 1932, 1 159; *C.A.* 23, 1677 (1934). (4) Likhoshesterov, *J. Am. Chem. Soc.* 54, 215-216 (1932); *Chem. Zvest.* 1932, 1 159; *C.A.* 23, 1677 (1934). (5) Likhoshesterov, *J. Am. Chem. Soc.* 54, 215-216 (1932); *Chem. Zvest.* 1932, 1 159; *C.A.* 23, 1677 (1934). (6) Likhoshesterov, *J. Am. Chem. Soc.* 54, 215-216 (1932); *Chem. Zvest.* 1932, 1 159; *C.A.* 23, 1677 (1934). (7) Likhoshesterov, *J. Am. Chem. Soc.* 54, 215-216 (1932); *Chem. Zvest.* 1932, 1 159; *C.A.* 23, 1677 (1934).



## 3:3400 1,3,7-TRICHLORONAPHTHALENE

 $C_{10}H_5Cl_3$ 

Beil. V-545

V<sub>1</sub>—V<sub>2</sub>—

M.P. 113° (1) (2) (3)

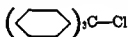
112.5-113° (4)

Ndls. from alc.

[For prepn. of  $\bar{C}$  from 1,3-dichloronaphthalenesulfonyl chloride-7 [Beil. XI-183] (5), from 1,7-dichloronaphthalenesulfonyl chloride-3 [Beil. XI-182] (6), from 3,7-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-162] (5), from 3-chloronaphthalene-1,7-bis-(sulfonyl chloride) [Beil. XI-215] (7), from 7-chloronaphthalene-1,3-bis-(sulfonyl chloride) [Beil. XI-212] (1) (3) (6) (7), from 1-nitronaphthalenedisulfonic acid-3,7 [Beil. XI-216] (3) (4), or from 7-chloro-3-naphtholsulfonic acid-1 (2), each with  $PCl_5$  as directed, see indic. refs.; for formn. of  $\bar{C}$  from  $\beta$ -chloronaphthalene tetrachloride (1,2,3,4,6-pentachlorotetralin) [Beil. V-493] with alc. KOH see (8).]

[ $\bar{C}$  treated with  $ClSO_3H$  in  $CS_2$  and reactn. prod. conv. to sodium salt as directed (1) yields sodium 1,3,7-trichloronaphthalenesulfonate-7 (corresp. sulfonyl chloride, m.p. 138° (1).]

3:3400 (1) Turner, Wynne, *J. Chem. Soc.* 1941, 247, 253-254. (2) Battegay, Silbermann, Kienzie, *Bull. soc. chim.* (4) 49, 718-719 (1931). (3) Armstrong, Wynne, *Chem. News* 61, 93 (1890). (4) Alén, *Ber.* 17, Referate, 437 (1884). (5) Armstrong, Wynne, *Chem. News* 61, 275 (1890). (6) Armstrong, Wynne, *Chem. News* 76, 69 (1879). (7) Armstrong, Wynne, *Chem. News* 62, 165 (1890). (8) Armstrong, Wynne, *Chem. News* 61, 285 (1890).

3:3410  $\alpha$ -CHLOROTRIPHENYL-METHANE $C_{19}H_{14}Cl$ 

Beil. V-700

V<sub>1</sub>-(346)V<sub>2</sub>-(615)

(Triphenylchloromethane;  
triphenylmethyl chloride;  
trityl chloride)

M.P. 113° (1)

112-113° (2) (3); cor. (8)

112° (4) (5) (6) (46)

111-112° (7) (9)

111° (10) (11)

110.5-112° (12)

110-112° (13)

110.0-110.5° (14)

100.2° (15)

109° (16)

109-110° (17)

108-112° (18)

108-111° (19)

106-109° (20)

106° (21) (50)

105-109° (30)

B.P. [310° at 20 mm. (22)]

230-235° at 20 mm. (23)

Colorless (12) or pale greenish-yellow (7) (8) cryst. from hexane +  $AcCl$  (1), dry ether (9), lgr. (7) (8), or dry  $C_6H_6$  + pet. ether (12) (17). — Ord.  $\bar{C}$  frequently conts. two kinds of crystals, white and yellow, both melting at 110-112° (13). —  $\bar{C}$  from  $CCl_4$  cryst. with

1 mole solvent;  $\bar{C}$  from acetone cryst. with  $\frac{1}{2}$  mole solvent; in both cases solvent is lost at 92° but not readily in air at ord. temp. (24). — [For study of x-ray crystallography of  $\bar{C}$  see (25).] — Note that  $\bar{C}$  cannot be recrystd. from MeOH or EtOH without more or less complete conversion to the corresp. trityl ethers (see also below under behavior of  $\bar{C}$  with alcohols).

$\bar{C}$  may be stored satisfactorily in ord. screw-top bottles, provided they are well sealed with paraffin (7) — On long exposure to moist air, however,  $\bar{C}$  is hydrolyzed (see also below) to triphenylcarbinol (1:5985), m.p. 161–162°; for f.p./compn. diagram of system  $\bar{C}$  + triphenylcarbinol, eutectic, m.p. 100°, contg. 90%  $\bar{C}$ , see (26). — Samples of partially hydrolyzed  $\bar{C}$  may be purified by recrystn. from  $\frac{1}{2}$  wt. of  $C_6H_6$  contg. 5–25% acetyl chloride, the latter reconverting the triphenylcarbinol to  $\bar{C}$  (7).

$\bar{C}$  is eas. sol. in ether,  $C_6H_6$  (100 g.  $C_6H_6$  dis. 85.8 g.  $\bar{C}$  at 25° (35)),  $CCl_4$ ,  $CHCl_3$ , or  $CS_2$ , but is much less sol. in pet. ether (19). — Solns. of  $\bar{C}$  in acetyl chloride (27) (29), benzoyl chloride (27), hot 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (27) (28), dichloroethylene (28), nitrobenzene (27),  $SOCl_2$  (27),  $SO_2Cl_2$  (29) are yellow; for study of effect of temp. see (27) — Solns. of  $\bar{C}$  in liq.  $SO_2$  are also yellow (29) and conduct electric current (30) (31) (32); for study of molecular weight of  $\bar{C}$  in liq.  $SO_2$  see (33). —  $\bar{C}$  is very sparingly sol. in liq.  $NH_3$  but soln. conducts elect. current (34).

[The protracted arguments on the constitution of  $\bar{C}$  and of trityl derivatives in general (controversy over carbonium and quinonoid forms, etc.) cannot be detailed within the scope of this book; however, for leading references since 1920 see (36) (37) (38) (39) (40) (41) (42) (43) (44) (45); for earlier references see Beil. V-700]

### PREPARATION OF $\bar{C}$

The two best-studied preparations of  $\bar{C}$  are those from triphenylcarbinol (1:5985) with  $AcCl$  (3:7065) in  $C_6H_6$  (93–95% yield (12)) and from  $CCl_4$  (3:5100) with  $C_6H_6$  +  $AlCl_3$  (84–86% yield on  $AlCl_3$  used (7) (8)). Note, however, that many other methods have also been used as recorded below.

From triphenylcarbinol (1:5985). [For prepn. of  $\bar{C}$  from triphenylcarbinol with  $AcCl$  (3:7065) directly (79% yield (16)) or in  $C_6H_6$  soln. (93–95% yield (12)); with oxalyl (dichloride) (3:5060) (47); with  $HCl$  gas in dry  $C_6H_6$  (48) (for study of equilibrium see (49)) contg.  $CaCl_2$  (9) or in dioxane at 50° for 22 hrs. (86% yield (14)); with conc.  $HCl$  in  $AcOH$  (79% yield (50)) or in  $C_6H_6$  +  $ZnCl_2$  (85% yield (51)); with  $PCl_5$  directly (52) or in lgr. (53) or in  $C_6H_6$  (29) or in  $C_6H_6$  +  $ZnCl_2$  (90% yield (51)); with  $PCl_5$  +  $ZnCl_2$  in  $C_6H_6$  (92% yield (51)); with  $SOCl_2$  in  $C_6H_6$  (97% yield (51)); with  $SiCl_4$  in  $C_6H_6$  or lgr. at 40° (54), or with  $COCl_2$  (3:5000) in  $C_6H_6$  +  $CaCl_2$  (5) see indic. refs.]

From other triphenylcarbinol derivatives. [For prepn. of  $\bar{C}$  from K triphenylcarbinolate with  $COCl_2$  (3:5000) in toluene (5); from triphenylmethoxy— $MgBr$ ,  $(C_6H_5)_3C-OMgBr$  (from benzophenone +  $C_6H_5MgBr$ ), with  $AcCl$  in  $C_6H_6$  (37% yield (55)) or with  $COCl_2$  in toluene (14% yield (55)); from triphenylcarbinol ethyl ether (see also below) with  $AlCl_3$  in  $CS_2$  (56) or with  $AcCl$  (46) (57) see indic. refs.]

From various other trityl derivatives and relatives. [For prepn. of  $\bar{C}$  from  $\alpha$ -bromotriphenylmethane (trityl bromide) with  $AgCl$  in  $C_6H_6$  in s.t. at 200° for several days (50% yield (57)); from  $\alpha$ -aminotriphenylmethane (tritylamine) [Beil. XII-1343, XII-(557)] with  $NH_4Cl$  in liq.  $NH_3$  (34), from triphenylmethylphosphinic acid  $[(C_6H_5)_3C(PO)(OH)]$  with  $PCl_5$  (3 moles) at 70° (91% yield (20)); from triphenylmethane (1:7220) with  $PCl_5$  at 160° for 2 hrs. (65% yield (58)) or with  $NOCl$  at 150° (59) see indic. refs.]

[For prepn. of  $\bar{C}$  from triphenylacetyl chloride [Beil. IX-713, IX-(309)] by loss of  $CO$  on htc. at 120–150° (60) or at 170–180° (61); from bis-(triphenylmethyl) peroxide [Beil.

VI-716, VI<sub>1</sub>-(350)] with Cl<sub>2</sub> + a little I<sub>2</sub> in boilg. CCl<sub>4</sub> soln. for 3 hrs. (40% yield (23)) see indic. refs.]

From benzene with various polyhalogenated methanes. [For prepn. of  $\bar{C}$  from C<sub>6</sub>H<sub>6</sub> (1:7400) with CCl<sub>4</sub> (3:5100) in pres. of AlCl<sub>3</sub> (84-86% yield on AlCl<sub>3</sub> used (7) (8); 70-85% yield (18)) cf. (62) (63) (64) in CS<sub>2</sub> (97% yield (19)) see indic. refs.; for use of FeCl<sub>3</sub> (31% yield against 77% with AlCl<sub>3</sub> under otherwise same conditions (10) cf. (65)) see indic. refs.]

[For prepn. of  $\bar{C}$  from C<sub>6</sub>H<sub>6</sub> (1:7400) with CHCl<sub>3</sub> (3:5050) + AlCl<sub>3</sub> at 50° see (22).]

[For formn. of  $\bar{C}$  from C<sub>6</sub>H<sub>6</sub> with dichloro-difluoro-methane ("Freon") + AlCl<sub>3</sub> see (66).]

From various chlorotoluenes. [For formn. of  $\bar{C}$  from benzotrichloride (3:6540) with C<sub>6</sub>H<sub>6</sub> in pres. of metallic U (67), Ti (68), Ce (69), or Cr (21) see indic. refs.; from benzal (di)chloride (3:6327) with C<sub>6</sub>H<sub>6</sub> + AlCl<sub>3</sub> see (22).]

From various chlorodiphenylmethanes. [For formn. of  $\bar{C}$  from  $\alpha$ -chlorodiphenylmethane (benzohydril chloride) (3:0060) (22) or from  $\alpha,\alpha$ -dichlorodiphenylmethane (benzophenone chloride) (3:6960) (70) with C<sub>6</sub>H<sub>6</sub> + AlCl<sub>3</sub> see indic. refs.]

From other miscellaneous sources. [For formn. of  $\bar{C}$  from pentaphenylethane [Beil. V-755, V<sub>1</sub>-(386), V<sub>2</sub>-(711)] with PCl<sub>5</sub> at 170° for 2 hrs. or refluxed in C<sub>6</sub>H<sub>6</sub> (58), or (together with other products) with HCl at 150° (71) or on evapn. of soln. in SO<sub>2</sub>Cl<sub>2</sub> (72).]

## CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis of  $\bar{C}$ .  $\bar{C}$  on htg. at 200° (52) (73) or 250° (53) or at 160° in pres. of P<sub>2</sub>O<sub>5</sub> (74) loses HCl and yields both triphenylmethane (1:7220), m.p. 92°, and 9-phenylfluorene [Beil. V-720, V<sub>1</sub>-(355), V<sub>2</sub>-(630)], m.p. 147-148°; note that 9-phenylfluorene is also formed from  $\bar{C}$  in various other reactions such as with POCl<sub>3</sub> on distn. (23) or with  $\frac{1}{10}$  wt. of mossy zinc refluxed in C<sub>6</sub>H<sub>6</sub> for 5 hrs. (75).

Reduction of  $\bar{C}$ .  $\bar{C}$  is reduced to triphenylmethane by many different types of reducing agent [e.g.,  $\bar{C}$  in anhydrous formic acid (1:1005) at 100° evolves CO<sub>2</sub> + HCl and gives (yield: 79% in 30 min., 90% in 2 hrs. (4)) triphenylmethane (1:7220);  $\bar{C}$  in EtOH treated with conc. H<sub>2</sub>SO<sub>4</sub> at 70-80° gives (76) (17) triphenylmethane accompanied by acetaldehyde (1:0100);  $\bar{C}$  is reduced by diethyl ether in the presence of AlCl<sub>3</sub> (56) (77), FeCl<sub>3</sub> (65), or ZnCl<sub>2</sub> (78) to triphenylmethane (1:7220), acetaldehyde (1:0100) and ethyl chloride (3:7015) also being formed; other reagents which effect reduction of  $\bar{C}$  to triphenylmethane (1:7220) include hydrazobenzene in boiling C<sub>6</sub>H<sub>6</sub> (79), cyclohexadiene-1,3 (dihydrobenzene) + HgCl<sub>2</sub> (80); Zn + AcOH (50) (reaction here is complex, and various other prods. may be formed according to conditions), and dry H<sub>2</sub>S at 150° (81)].

Oxidation of  $\bar{C}$ .  $\bar{C}$  is not readily oxidized:  $\bar{C}$  with silver oxide in dry C<sub>6</sub>H<sub>6</sub> or ether gives (78) a little fuchson, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>=C<sub>6</sub>H<sub>4</sub>=O [Beil. VII-520, VII<sub>1</sub>-(290)], m.p. 168°, together with other amorphous products difficult to purify; note, however, that  $\bar{C}$  in alcohol-free acetone with KMnO<sub>4</sub> in same solvent instantly reduces the KMnO<sub>4</sub> and gives (100% yield (85)) triphenylcarbinol (1:5985).

Hydrolysis of  $\bar{C}$ .  $\bar{C}$  with aq. hydrolyzes to triphenylcarbinol (1:5985) + HCl: e.g.,  $\bar{C}$  on shaking with aq. at ord. temp. is 85% hydrolyzed in 48 hrs. (26) cf. (82) (83) (in this connection note m.p./compn. diagram (26) of  $\bar{C}$  + triphenylcarbinol);  $\bar{C}$  with boilg. aq. rapidly and completely yields only triphenylcarbinol.

[For study of hydrolysis of  $\bar{C}$  by aq. in acetone (84), in dioxane (14), or by aq. HCl (35) see indic. refs.]

$\bar{C}$  dissolves in cold conc. H<sub>2</sub>SO<sub>4</sub> yielding (86) (48) (87) a golden-yellow soln. with evolution of HCl (88) (86) (48) and formn. of triphenylcarbinyl hydrogen sulfate; dilution of this soln. with aq. ppts. (99% yield (86) (48)) triphenylcarbinol (1:5985).

$\bar{C}$  dissolves in phenol with deep brown color; on dilution of the freshly prepd. soln. with aq. it becomes colorless and both HCl and triphenylcarbinol are detectable; if, however, the phenol soln. has stood for some time prior to dilution some *p*-tritylphenol [Beil. VI-731, VI<sub>1</sub>-(364)], m.p. 282°, is also formed (89) (see also below under behavior of  $\bar{C}$  with phenols).]

## BEHAVIOR OF $\bar{C}$ WITH OTHER INORGANIC REACTANTS

### WITH SALTS OF VARIOUS INORGANIC ACIDS

#### With Salts of Hydrogen Peroxide

$\bar{C}$  in acetone with 30%  $H_2O_2$  in freezing mixt. treated with 50% KOH gives (90) trityl hydroperoxide,  $(C_6H_5)_3C-O-OH$  (isolated as its addn. cpd. with pyridine hydrochloride, viz.,  $(C_6H_5)_3C-O-OH \cdot C_5H_5N \cdot HCl$ , cryst. from alc., m.p. 133° dec.), accompanied by some triphenylcarbinol (1:5985).]

$\bar{C}$  in  $C_6H_6$  with aq.  $Na_2O_2$  as directed (91) gives (5-11% yield) bis-trityl peroxide,  $(C_6H_5)_3C-O-O-C(C_6H_5)_3$ , cryst. from hot  $CS_2$ , m.p. 185-186°, accompanied by much triphenylcarbinol; the bis-trityl peroxide is also obtainable from the trityl hydroperoxide (above) by reaction with  $\bar{C}$  in  $C_6H_6$  on addn. of aq. alk. (90).]

#### With Salts of Halogen Hydrides

With alkali or alkaline-earth salts.  $\bar{C}$  with alkali fluorides seems not to have been studied; note, however, that trityl fluoride, cryst. from  $CCl_4$ , m.p. 104° (6), has been prepd. by other means, viz., from triphenylcarbinol with HF (6) or with acetyl fluoride (85).]

$\bar{C}$  with anhydrous  $CaBr_2$  in  $C_6H_6$  at room temp. for 5-6 hrs. (92) or  $\bar{C}$  with HBr in  $C_6H_6$  at room temp. for 20 hrs. (92) is largely converted to trityl bromide [Beil. V-704, V<sub>1</sub>-(348), V<sub>2</sub>-(617)], m.p. 152°.]

[For study of rate of reaction of  $\bar{C}$  with KI in dry acetone at 0° see (93); note, however, that, although trityl iodide [Beil. V-706], m.p. 132°, is doubtless formed, yet more or less sepn. of  $I_2$  and formn. of triphenylmethyl (or its reaction prods.) occurs also.]

With metal chlorides.  $\bar{C}$  with many metallic chlorides forms double salts [e.g.,  $\bar{C}$  with  $AlCl_3$  forms (19) (87) a cpd.,  $\bar{C} \cdot AlCl_3$ , dark-yellow very hygroscopic cryst. from nitrobenzene +  $CS_2$ , dec. abt. 122-125°;  $\bar{C}$  in nitrobenzene with  $SnCl_4$  gives on addn. of dry  $CS_2$  or.-yel. cryst. of a cpd.,  $\bar{C} \cdot SnCl_4$  (30) (57) (87) (94);  $\bar{C}$  with  $SbCl_5$  gives (57) a cpd.,  $\bar{C} \cdot SbCl_5$ , red cryst.;  $\bar{C}$  with  $BCl_3$  gives a cpd.,  $\bar{C} \cdot BCl_3$  (6), etc.].

#### With Salts of Hydrogen Sulfide

$\bar{C}$  with alc. NaSH (from alc. NaOEt sdd. with  $H_2S$ ) (81) cf. (95) (96), or  $\bar{C}$  with KSF in  $C_6H_6$  (96), gives triphenylthiocarbinol [Beil. VI<sub>1</sub>-(352)], cryst. from abs. alc. or alc. +  $CHCl_3$ , m.p. 107° (81) (95) —  $\bar{C}$  with alc.  $Na_2S$  as directed gives (21% yield (95)) bis-trityl sulfide, m.p. 182° dec. — Note also that bis-trityl disulfide, cryst. from  $C_6H_6$  + pet. ether, m.p. 157° dec. (95) [Beil. VI<sub>1</sub>-(353)], is also known but prepd. indirectly (81) (95) (96).]

#### With Other Salts of Inorganic Acids

$\bar{C}$  with  $Ag_2SO_4$  in liq.  $SO_2$  (23),  $C_6H_6$  (97), or at 120-130° for 15-20 min. (98) cf. (48) gives di-trityl sulfate [Beil. VI-717, VI<sub>1</sub>-(351)]. —  $\bar{C}$  with  $AgClO_4$  in nitrobenzene +  $C_6H_6$  gives (99) trityl perchlorate [Beil. VI-717, VI<sub>1</sub>-(351)]. —  $\bar{C}$  with  $AgCrO_4$  in  $C_6H_6$  gives (48) cf. (100) di-trityl chromate [Beil. VI-717; note that this salt is also obtd. from  $\bar{C}$  with  $CrO_3$  in  $C_6H_6$  or  $CCl_4$  (101).]

[ $\bar{C}$  with  $\text{NaN}_3$  in  $\text{C}_6\text{H}_6$  refluxed 20 hrs. gives (100% yield (102)) trityl azide [Beil. V-708, V<sub>1</sub>-(349), V<sub>2</sub>-(618)], colorless cryst., m.p. 64° (102), 65° (103). — For study of reaction of  $\bar{C}$  with silver hyponitrite and decompn. of the transient trityl hyponitrite see (104)]

#### WITH METAL OXIDES

[ $\bar{C}$  with  $\text{HgO}$  in dry  $\text{C}_6\text{H}_6$ , ether,  $\text{CS}_2$ , or  $\text{CHCl}_3$  as directed (78) cf. (105) (106) gives (50–85% yield (78)) di-trityl oxide, cryst. from xylene, m.p. 237–238° (106), 235–237° (78) (105). — Note that  $\bar{C}$  with  $\text{Ag}_2\text{O}$  in  $\text{C}_6\text{H}_6$  undergoes oxidation (cf. above); note that  $\bar{C}$  with  $\text{CrO}_3$  in  $\text{C}_6\text{H}_6$  or  $\text{CCl}_4$  gives (101) di-trityl chromate [Beil. VI-717].]

#### WITH METALS

With alkali metals (or their amalgams). [ $\bar{C}$  in dry ether with 1%  $\text{Na}/\text{Hg}$  on shaking at room temp. (2) (8) (107) (108) (109) or  $\bar{C}$  with  $\text{Na}$  in liq.  $\text{NH}_3$  (112) gives tritylsodium (sodium triphenylmethyl) [Beil. XVI<sub>1</sub>-(589)].  $\bar{C}$  with  $\text{K}$  in liq.  $\text{NH}_3$  gives (112) tritylpotassium. —  $\bar{C}$  in dry ether with excess  $\text{Li}/\text{Hg}$ ,  $\text{Rb}/\text{Hg}$ , or  $\text{Cs}/\text{Hg}$  in absence of air gives (113) corresp. trityllithium, tritylrubidium, or tritylcesium. — For behavior of  $\bar{C}$  with calcium in liq.  $\text{NH}_3$  see (112). — In this connection note that  $\bar{C}$  in dry ether,  $\text{C}_6\text{H}_6$ , or  $\text{CS}_2$  in absence of air and under  $\text{CO}_2$  with molecular  $\text{Ag}$  (91) cf. (117),  $\text{Hg}$  (91),  $\text{Zn}$  (91) (114) (115), or  $\bar{C}$  with  $\text{Cu}$  bronze in  $\text{C}_6\text{H}_6$  +  $\text{EtOAc}$  (116) or in s.t. at 80–110° in dark (117) gives triphenylmethyl (trityl); note also that  $\bar{C}$  with  $\text{Zn}$  +  $\text{AcOH}$  in the cold gives (50) triphenylmethane (1:7220) + trityl, but the same mixture if heated gives triphenylmethane + 1-benzohydril-4-tritylbenzene [Beil. V-761], m.p. 231° (118), 230° cor. (110), the latter under certain conditions attaining as high as 70% (50) (118).]

With  $\text{Zn}$ . [ $\bar{C}$  with  $\frac{1}{10}$  wt. of mossy zinc refluxed in  $\text{C}_6\text{H}_6$  for 5 hrs. gives (75) 9-phenylfluorene (see also above under pyrolysis of  $\bar{C}$ ). — For behavior of  $\bar{C}$  with  $\text{Zn}$  in  $\text{EtOAc}$  see (120).]

With  $\text{Mg}$  (in dry ether).  $\bar{C}$  with  $\text{Mg}$  in dry ether in the pres. of  $\text{I}_2$  as directed gives (96% yield (13)) cf. (121) of corresp.  $\text{R}-\text{Mg}-\text{Cl}$  cpd., viz., trityl- $\text{Mg}-\text{Cl}$  [Beil. XVI-942, XVI<sub>1</sub>-(556)]. — [The former controversy as to whether this can exist in a more reactive quinonoid structure ( $\alpha$ ) or a relatively less reactive carbonium ( $\beta$ ) structure cannot be reported here (for references see above Beilstein citation), nor can space be taken for a full account of its reactions.] — Note, however, that this  $\text{RMgCl}$  cpd. with  $\text{CO}_2$  gives (yields: 91% (2), 87.5% (121)) (122) (59) triphenylacetic acid [Beil. IX-712, IX<sub>1</sub>-(309)], m.p. 264–265° dec. (122); for study of adverse influence of triphenylcarbinol or of benzaldehyde see (121).]

#### WITH NITROGENOUS INORGANIC REACTANTS

[ $\bar{C}$  dislvd. in  $\text{C}_6\text{H}_6$  and satd. with dry  $\text{NH}_3$  gas (123) (124) repeatedly (125), or  $\bar{C}$  in naphthalene with dry  $\text{NH}_3$  gas at 130° (126), gives (45% yield (126)) tritylamine (triphenylmethyl-amine) [Beil. XII-1343, XII<sub>1</sub>-(557)], pr. from abs. alc., m.p. 102° (126), 103–104° (124), 105° (127) (corresp.  $\text{B.HCl}$ , spar. sol. aq., m.p. 244° (127)).]

[ $\bar{C}$  with  $\text{NH}_2\text{OH}$  (from  $\text{NH}_2\text{OH.HCl}$  in  $\text{MeOH}/\text{NaOMe}$ ) in  $\text{C}_6\text{H}_6$  gives (73–75% yield (3)) (128) cf. (129) *N*-tritylhydroxylamine [Beil. XV-33, XV<sub>1</sub>-(11)], pr. from  $\text{C}_6\text{H}_5/\text{pet. ether}$ , m.p. 130–135° (3), 124–135° u.c. (128); for study of rearr. of this prod. see (129). — For study of *N*-methyl ether of this prod., viz., *N*-trityl-*N*-methylhydroxylamine (similarly prepd. from  $\bar{C}$  with *N*-methylhydroxylamine) see (130) (131); for study of the isomeric *O*-methyl ether, viz., *N*-trityl-*O*-methylhydroxylamine (from  $\bar{C}$  with methoxyamine), see (132).]

[ $\bar{C}$  with hydrazine hydrate (2 moles) in alc. at ord. temp. (232) or in dry ether under reflux (233) or in dry pyridine at 45–50° (234) gives (63% yield (234)) *N,N'*-di-tritylhydrazine]

zinc ( $\alpha, \alpha'$ -hydrazotriphenylmethane) [Beil. XV-582, XV<sub>1</sub>-(184)], m.p. 212° (234), 219-220° dec. (235), often accompanied (232) (233) by some *N*-tritylhydrazine [Beil. XV-591, XV<sub>1</sub>-(184)]

## BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

### WITH ORGANIC HYDROXY OR MERCAPTO COMPOUNDS

#### With Alcohols

$\bar{C}$  with alcohols gives the corresp. ethers of triphenylcarbinol. With the lower monohydric alcs this conversion can occur merely on solution and warming, but higher alcs. usually require htg., use of metal alcoholate, use of an acid acceptor (pyridine), etc.

With methyl alcohol.  $\bar{C}$  with MeOH (1:6120) in  $C_6H_6$  for 10 min. (133), or  $\bar{C}$  with MeOH/NaOMe refluxed 4 hrs. (134), gives (55% yield (134)) triphenylcarbinyl methyl ether ( $\alpha$ -methoxytriphenylmethane), cryst. from MeOH, m.p. 83.5-84° (133), 82.5-83° (134), 82.6-82.9° (134) (136), 82° (64); note, however, that this product exists in dimorphous forms; the lower-melting form just mentioned sometimes (134) (135) changes to a higher-melting form, m.p. 96.0-96.5° (134) (135); note also that the m.p. of this methyl ether is close to that of the ethyl ether (see below) but that a mixed m.p. of the two is depressed (136). — [For studies of hydrolysis of the methyl trityl ether to triphenylmethane (1:7220) and formaldehyde (1:0145) see (134) (136); for prepn. of its addn. cpd., m.p. 90-91°, with PhOH see (138)]

With ethyl alcohol.  $\bar{C}$  with abs. EtOH (1:6130) on warming (1) (4) (5) (52) or even shaking 1 min. nt ord. temp. (139), or  $\bar{C}$  with nbs. EtOH/NaOEt (9) (56) (134) (139), gives (yields: 83% (138), 50% (134)) triphenylcarbinyl ethyl ether ( $\alpha$ -ethoxytriphenylmethane), cryst. from nbs. alc., ether, or pet. ether, m.p. 84° (5), 83° (1) (9), 81.2-81.8° (134), 81.3° (56), 81° (4). — Note that the m.p. of this prod. is almost identical with that of triphenylcarbinyl methyl ether (above) but that a mixed m.p. of the two is depressed (137). — [For study of pyrolysis of this ethyl trityl ether yielding triphenylmethane (1:7220) and acetaldehyde see (134) (136); for study of its cleavage with AcCl (3:7065) (57) (46), with AlCl<sub>3</sub> in CS<sub>2</sub> (56), or with EtOH/HCl (26) see indic. refs.; for conversion with boilg. anhydrous formic acid to triphenylmethane (1:7220) see (4).]

With other monohydric alcs.  $\bar{C}$  with *n*-PrOH (1:6150) in dry pyridine nt room temp. for 20 hrs. (140), or  $\bar{C}$  with *n*-PrOH/NaO *n*-Pr refluxed 4 hrs. (134), gives (10% yield (134)) trityl *n*-propyl ether, cryst. from *n*-PrOH/pet. ether, m.p. 55° (140), 50.5-52.5° (134). —  $\bar{C}$  with isopropyl alc. (1:6135) in dry pyridine nt room temp. for 20 hrs. (140) or  $\bar{C}$  with isopropyl alc./Na isopropylate under reflux gives (50% yield (134)) trityl isopropyl ether, m.p. 113° (140), 112.9-113.8° (134), 111.7° (56). —  $\bar{C}$  with *n*-BuOH (1:6180) + sodium *n*-butylate gives (40% yield (134)) trityl *n*-butyl ether, oil, b.p. 196-199° nt 5 mm. (134). — For prepn. of corresp. trityl ethers from *sec*-butyl alc. (1:6155) (134), isobutyl alc. (1:6165) (134), isomyl alc. (1:6200) (134), cetyl alc. (1:5915) (140), allyl alc. (1:6145) (140), benzyl alc. (1:6450) (134), cyclohexanol (1:6415) (140), see indic. refs.]

[For prepn. of corresp. trityl ethers from *l*-menthol (1:5940) (152) (153) (154), *d*-borneol (1:5990) (152) (153), or cholesterol (1:5975) (152) see indic. refs.]

[Note, however, that  $\bar{C}$  with K triphenylcarbinolate does not give the expected prod. but rather (96) *p*-hydroxytriphenylcarbinol in the form of its anhydride fuchsone; the expected ditrityl ether has been obtd. from  $\bar{C}$  by action of HgO (see above).]

With various important substituted monohydric alcohols.  $\bar{C}$  with  $\beta$ -methoxyethanol (methyl "cellosolve") (1:6405) in pyridine gives (80-85% yield (141)) trityl  $\beta$ -methoxyethyl ether, m.p. 105.5-106.0° u.c. (141), 104° (142). —  $\bar{C}$  with  $\beta$ -ethoxyethanol ("cellosolve") (1:6410) in pyridine nt 100° for 5 hrs. gives (92% yield (141)) trityl  $\beta$ -ethoxyethyl

ether, m.p. 79.0-79.5° u.c. (141), 77-78° (143). —  $\bar{C}$  with  $\beta$ -isopropoxyethyl alc. (isopropyl "cellosolve") (1:6413) in pyridine gives (50-60% yield (141)) trityl  $\beta$ -isopropoxyethyl ether, m.p. 71.0-71.5° u.c. (141). —  $\bar{C}$  with  $\beta$ -benzyloxyethyl alc. (benzyl "cellosolve") (1:6533) in pyridine gives (50-70% yield (141)) trityl  $\beta$ -benzyloxyethyl ether, m.p. 76-77° u.c. (141). —  $\bar{C}$  with  $\beta$ -phenoxyethyl alc. (phenyl "cellosolve") (1:6518) in pyridine gives (75-85% yield (141)) trityl  $\beta$ -phenoxyethyl ether, m.p. 123.5-124.0° u.c. (141).]

[ $\bar{C}$  with  $\beta$ -( $\beta$ -methoxyethoxy)ethyl alc. (methyl "carbitol") (1:6458) in pyridine gives (55-60% yield (141)) trityl  $\beta$ -( $\beta$ -methoxyethoxy)ethyl ether, m.p. 58-59° u.c. (141). — Note that the trityl ethers of  $\beta$ -( $\beta$ -ethoxyethoxy)ethyl alc. ("carbitol") (1:6470) and of  $\beta$ -( $\beta$ -n-butoxyethoxy)ethyl alc. (butyl "carbitol") (1:6517) are unreported.]

With various polyhydric alcohols. (For  $\bar{C}$  with carbohydrates see separate section below.)

[ $\bar{C}$  with ethylene glycol (1:6465) in pyridine may according to conditions (141) give either or both of the two possible ethers, viz., ethylene glycol monotrityl ether, m.p. 105-105.5° u.c. (141), 104.5-105.5° (141), 102-103° (143), 98-100° (140) (corresp. benzoyl deriv. m.p. 58.5-59.5° (144); corresp. *p*-nitrobenzoyl deriv., m.p. 155-156° (144)), and/or ethylene glycol ditrityl ether, m.p. 190° u.c. (145), 187-188° u.c. (141), 185-186° (140)]

[ $\bar{C}$  with propylene glycol (propanediol-1,2) (1:6455) in pyridine gives (146) propylene glycol ditrityl ether, m.p. 176.5-177.0° u.c. (146).]

[ $\bar{C}$  (2 moles) with diethylene glycol (1:6525) in pyridine gives (60-70% yield (141)) diethylene glycol ditrityl ether, m.p. 157.5-158.0° u.c. (141); note that corresp. diethylene glycol monotrityl ether has m.p. 112.5-113.5° u.c. (141).]

[ $\bar{C}$  (2 moles) with triethylene glycol (1:6538) in pyridine gives (45-60% yield (141)) triethylene glycol ditrityl ether, m.p. 142.0-142.5° u.c. (141); note that this prod. is dimorphous, and an unstable form, m.p. 130.5-131.5° u.c., sometimes obt'd. can be converted to the stable higher-melting form by htg. at 125° or by grinding in acetone (141).]

[ $\bar{C}$  with glycerol (1:6540) may give mono-, di-, or tritryl ethers acc. to conditions; glycerol  $\alpha$ -monotrityl ether, m.p. 93-94° (147), 92-94° (140), but also sometimes in another form of m.p. 108-110° (147) (148), 109-110° (149); glycerol  $\alpha,\alpha'$ -ditrityl ether, m.p. 174-177° (150), 174-176° cor. (151), 170-171° (140); glycerol  $\alpha,\alpha',\beta$ -tris-trityl ether, m.p. 196-197° (147) (150). — Note that the relationships of these three ethers are subtle; e.g., the monoether at 180-190° is converted (147) into the  $\alpha,\alpha'$ -diether; the latter in turn at 260° gives (147) the triether.]

[ $\bar{C}$  (4 moles) with pentaerythritol (1:5850) in pyridine gives (145) a tetratrityl ether m.p. above 350°.]

With carbohydrates and their relatives.  $\bar{C}$  has recently been much employed as a tritylating agent for compounds of the carbohydrate group. This use started from the original (erroneous) impression that  $\bar{C}$  etherified hydroxyl groups only if the latter were primary. However, although  $\bar{C}$  does in general react preferentially with such primary hydroxyls, and this reaction has been proposed (155) as a means for the detection of primary alcs. in the presence of secondary and/or tertiary alcohols, yet such primary tritylation is *not* specific. Abundant evidence is already available (156) (157) (158) (159) that secondary hydroxyl groups undergo tritylation. Although the scope of this book cannot be extended to a detailed treatment of the use of  $\bar{C}$  as tritylating agent in the carbohydrate group, yet a few brief citations may be of service as leading references.

With various tetrahydric alcohols. [For behavior of  $\bar{C}$  with *meso*-erythritol (1:5825) and pentaerythritol (1:5850) see (145).]

With various pentahydric alcohols and pentoses. [For behavior of  $\bar{C}$  with adonitol, arabit, xylitol, fucitol, rhamnitol, and epirhamnitol see (145); with arabinose, ribose, and xylose see (160); with various derivatives of these see (158) (167) (168).]





type (104)) accompanied by a trace of a cryptophenol, presumably 2-trityl-4-methylphenol, m.p. 182° (185) (190), also nhtd. (64% yield (190)) from  $\bar{C}$  with sodium *p*-cresolate in excess *p*-cresol at 130–140° for 3 hrs.]

*With other phenols.* [For further examples of nuclear tritylation of phenols by use of  $\bar{C}$  with isochavihetol and isoeugenol see (196) cf. (26); with 2-hydroxynaphthoquinone-1,4 see (197). — For formn. of di-trityl ethers from pyrocatechol (1:1520) (140) or from hydroquinone (1:1590) (108) see indie. refs.]

*With thiophenols.*  $\bar{C}$  with thiophenol on hgt. (109) or in  $C_6H_6$  soln. on refluxing  $\frac{1}{2}$  hr. (180) (179), or  $\bar{C}$  with  $NaSC_6H_5$  in ether at ord. temp. for 18 hrs. (200) (201), gives (yield alm. quant. (109) (200), 96% (180)) trityl phenyl sulfide, m.p. 106.5° (180), 106° (201), 105–106° (199) (200), 105° (179); this prod. on oxidn. with  $CrO_3/AcOH$  gives (199) the corresp. sulfoxide, m.p. 163°, but is unaffected by  $H_2O_2$  (199) [for corresp. sulfone, m.p. 175–176° (210), see below under reaction of  $\bar{C}$  with salts of organic acids (sodium benzene-sulfinate)].

[For corresp. sulfides from  $\bar{C}$  with *o*-thiocresol, *p*-thiocresol,  $\alpha$ -thionaphthol,  $\beta$ -thionaphthol, 2,4-dinitrothiophenol see (201).]

*With enols or enolates.* [For examples of reaction of  $\bar{C}$  with the enol form of diphenylacetaldehyde (202), methyl diphenylacetate (202), or with stilbenediol *bis*-MgI cpd. (203) see indie. refs.]

#### BEHAVIOR OF $\bar{C}$ WITH ETHERS

$\bar{C}$  with various aliphatic ethers in the pres. of suitable catalysts yields triphenylmethane and an aldehyde [e.g.,  $\bar{C}$  with diethyl ether in the pres. of  $AlCl_3$  (56) (77),  $FeCl_3$  (65), or  $ZnCl_2$  (78) gives triphenylmethane and acetaldehyde; although the latter is lost by polymerization the method is standard (77) for prepn. of triphenylmethane (1:7220)].

[Note, however, that with aromatic ethers nuclear tritylation occurs: e.g.,  $\bar{C}$  with anisole (1:7445) +  $SnCl_4$  at 100–110° for 1 hr. gives (45% yield (204)) 4-tritylanisole; m.p. 200.5° (204).]

#### BEHAVIOR OF $\bar{C}$ WITH ORGANIC ACIDS

(For salts of organic acids see below.)

$\bar{C}$  with  $AcOH$  even at 13° (133) (146) cf. (50) is in equilibrium with trityl acetate (see below) +  $HCl$ . —  $\bar{C}$  with thiolacetic acid ( $CH_3COSH$ ) gives trityl thiolacetate [Beil. VI-721, VI<sub>1</sub>-(353)], m.p. 138° (179). —  $\bar{C}$  with thiolbenzoic acid ( $C_6H_5COSH$ ) in toluene gives (85% yield (180)) trityl thiolbenzoate [Beil. IX-422, IX<sub>1</sub>-(170)], m.p. 187.5–188° (180). —  $\bar{C}$  with free thiocyanic acid in  $C_6H_6$  gives (97% yield (180)) trityl thiocyanate, m.p. 139° (180) (see also below).

#### BEHAVIOR OF $\bar{C}$ WITH SALTS OF ORGANIC ACIDS

$\bar{C}$  with salts of organic acids normally reacts to yield the corresp. trityl esters.

$\bar{C}$  with  $AgOAc$  in dry ether or  $C_6H_6$  on shaking at room temp. (57) or in  $C_6H_6$  refluxed 2 hrs. (46), or  $\bar{C}$  shaken with  $NH_4OAc$  in  $C_6H_6$  at ord. temp. (205), gives trityl acetate, cryst. from  $AcOEt$  + lgr., m.p. 87–88° (46) (57). —  $\bar{C}$  with  $AgOBz$  in  $C_6H_6$  at 60° for 4 hrs. gives (96) trityl benzoate, m.p. 165–166° (96). — Note that in analogous fashion  $\bar{C}$  might be expected to react with silver salts of *p*-nitrobenzoic and 3,5-dinitrobenzoic acids to give corresp. esters, but these are unreported.

[ $\bar{C}$  with excess dry  $Ag_2CO_3$  in dry  $C_6H_6$  shaken 24 hrs. gives (60–80% yield (106)) (105) ditrityl carbonate, cryst. from xylene, m.p. 209° dec. (106), 205–210° (105); this prod. on hgt. in xylene in pres. of  $Cu$  pdr. decomposes (106) (105) into  $CO_2$  and ditrityl ether, m.p. 237–238° (106) (see also above under  $\bar{C}$  with  $HgO$ ).]

[ $\bar{C}$  with excess  $Hg(CN)_2$  at 150–170° for 1 hr. gives (alm. 100% yield (53)) on extraction

with  $C_6H_6$  (53) (206) (207) trityl cyanide (triphenylacetoneitrile) [Beil. IX-714, IX<sub>1</sub>-(309)], pr. from AcOH, m.p. 129° (208), 127.5° (53) ]

[ $\bar{C}$  with mercury fulminate in dry  $C_6H_6$  under cooling gives (85% yield (208)) trityl cyanide oxide,  $(C_6H_5)_3CNO$ , ndls. from alc., m.p. 153-154° (208) ]

[ $\bar{C}$  with KSCN in dry  $C_6H_6$  shaken at room temp. for 2 days gives (209) trityl thiocyanate [Beil. VI-721], m.p. 137° (209) (see also above under  $\bar{C}$  with organic acids (HSCN)).]

[ $\bar{C}$  with sodium benzenesulfinate in dry ether gives (210) trityl phenyl sulfone [Beil. VI-721], lfts. from ether, m.p. 175-176° (210); note that corresp. sulfoxide (see above under behavior of  $\bar{C}$  with thiophenol) has m.p. 163°. — Similarly,  $\bar{C}$  with sodium *p*-toluenesulfinate in dry  $C_6H_6$  gives (179) trityl *p*-tolyl sulfone [Beil. VI-(353)], m.p. 173° (179).]

### BEHAVIOR OF $\bar{C}$ WITH ORGANOMETALLIC COMPOUNDS

This topic cannot be fully expanded within the scope of this book, but the following examples will serve as leading references.

With organo-alkali compounds. [ $\bar{C}$  with Li *n*-butyl in pet. ether for 9 days gives (26% yield (211)) 1,1,1-triphenylpentaoe, m.p. 153-154° (211) —  $\bar{C}$  with Li  $C_6H_5$  gives (212) free trityl isolated in form of (20% yield) ditrityl peroxide ]

[ $\bar{C}$  with Na *n*-butyl or Na trityl in liq.  $NH_3$  + toluene (112) or  $\bar{C}$  with Na trityl in dry ether (108) gives free trityl. —  $\bar{C}$  with Na + tetraphenylethylene as directed gives (213) pentaphenylethyl ]

With  $RMgX$  compounds.  $\bar{C}$  with  $MeMgBr$  (214) or  $\bar{C}$  with  $MeMgI$  (215) gives no gas (216) cf. (217) (218) but couples giving (yields: 95% (214), 70% (215)) 1,1,1-triphenylethane ( $\alpha$ -methyltriphenylmethane) [Beil. V-709, V<sub>1</sub>-(350)], cryst. from alc., m.p. 94-95° (214) (215), 94.8-95.0° (15); note that this prod. is also obtd. from  $MeMgBr$  with trityl acetate (61% yield (219)) or from K trityl with  $MeI$  in liq.  $NH_3$  (85-94% yield (220)).]

[ $\bar{C}$  with  $EtMgBr$  in dry ether reacts rapidly and quant. (221) yielding (215) not only the expected 1,1,1-triphenylpropane [Beil. V-712], m.p. 51° (215), but also (215) triphenylmethane (1:7220) and ethylene ]

[ $\bar{C}$  with *n*- $PrMgBr$  in dry ether gives (215) not only 1,1,1-triphenylbutane, m.p. 79° (215), but also considerable triphenylmethane (1:7220). —  $\bar{C}$  with *iso*- $PrMgBr$  in dry ether gives (215) not only 1,1,1-triphenyl-2-methylpropane, b.p. 233-234° at 21 mm. (215), but also much triphenylmethane (1:7220).]

[ $\bar{C}$  with  $C_6H_5MgBr$  in dry ether or  $C_6H_6$  gives a small yield (25-30% (222), 10-12% (139), 5-10% (215) (223)) tetraphenylmethane [Beil. V-738, V<sub>1</sub>-(371), V<sub>2</sub>-(672)], m.p. 281-282° (224) (225), b.p. 431° at 760 mm. (225), but the principal product (yield: 50-77% (222), 47.4% (226)) is 4-benzohydrylbiphenyl (*p*-phenyltetraphenylmethane) [Beil. V-738, V<sub>2</sub>-(672)], m.p. 111° (226), 112-113° (116); for explanation and study of this reaction see (222) — Note that  $\bar{C}$  with  $C_6H_5MgI$  behaves differently giving (227) cf. (179) triphenylmethyl and biphenyl (1:7175) ]

[ $\bar{C}$  in  $C_6H_6$  with benzyl  $MgCl$  in dry ether gives (100% yield (215)) (228) 1,1,1,2-tetraphenylethane [Beil. V-740, V<sub>1</sub>-(372), V<sub>2</sub>-(674)], m.p. 144° (215), 143.5-143.7° (15). —  $\bar{C}$  with benzohydryl bromide +  $Mg$  in dry ether (215) cf. (230) (or better trityl  $MgBr$  + benzohydryl bromide (229) cf. (230)) gives (90% yield (229)) pentaphenylethane [Beil. V-755, V<sub>1</sub>-(386), V<sub>2</sub>-(711)], m.p. in air 166-178° (229), in  $N_2$  182-185° (229). —  $\bar{C}$  with trityl  $MgCl$  gives (230) free trityl.]

[For behavior of  $\bar{C}$  with phenylacetylenyl  $MgBr$  giving trityl-phenylacetylene or with acetylene-*bis*- $MgBr$  giving di-tritylacetylene (hexaphenylbutyne-2) see (231).]

BEHAVIOR OF  $\bar{C}$  WITH (ORGANIC) AMINES

(For  $\bar{C}$  with  $NH_3$ ,  $NH_2OH$ ,  $NH_2NH_2$ , etc., see above under  $\bar{C}$  with inorganic nitrogen compds; for  $\bar{C}$  with arylhydrazines see below.)

 $\bar{C}$  with Primary Amines

[ $\bar{C}$  with  $MeNH_2$  in  $C_6H_6$  in pres. of  $NaOMe$  gives (125) trityl-*N*-methylaniline [Beil. XII-1344, XII<sub>1</sub>-(557)], m.p. 73° (125) (236) (corresp.  $\bar{B} \cdot HCl$ , m.p. 216° (125)).]

With aromatic *prim.* amines.  $\bar{C}$  in  $C_6H_6$  with aniline in alc. refluxed 15 min. gives (80% yield (228)) (57) *N*-tritylaniline [Beil. XII-1344, XII<sub>1</sub>-(557)], cryst. from alc / ether, m.p. 149–150° (57), 148–149° (237), 146° (228) [note that this prod. with  $\frac{1}{2}$  its wt.  $ZnCl_2$  at 160° for 15 min. rearranges (228) to *p*-tritylaniline [Beil. XII-1348], ndls. from toluene or alc., m.p. 256° cor. (225), 249° (228); note also that  $\bar{C}$  is claimed to form with aniline an addn. epd., m.p. 189–190° (34)].

[ $\bar{C}$  in  $C_6H_6$  with *o*-toluidine in alc. refluxed 15 min. gives (228) *N*-trityl-*o*-toluidine, m.p. 142.5° (228), 142° (237) (238), 140–142° (57); this prod. with  $ZnCl_2$  at 160° for 15 min. rearranges (82% yield (189)) (228) to 4-trityl-2-methylaniline, m.p. 216° (228), 215° (189) (not to  $\alpha$ -(2-amino)- $\beta,\beta,\beta$ -triphenylethane as originally supposed (228) cf. (189)). —  $\bar{C}$  with *m*-toluidine directly has not been studied nor has the other expected product, viz., *N*-trityl-*m*-toluidine, nor its rearr. prod., been reported. —  $\bar{C}$  in  $C_6H_6$  with *p*-toluidine in alc. refluxed 15 min. gives (228) *N*-trityl-*p*-toluidine [Beil. XII-1344], m.p. 180° (228), 177–178° (85), 177° (238), 176° (237): this product with  $ZnCl_2$  at 190° for 30 min. does not (228) rearrange.]

[ $\bar{C}$  with *p*-aminobiphenyl (*p*-xenylamine) in  $C_6H_6$  on htg. gives (82% yield (239)) *N*-trityl-*p*-xenylamine, pr. from  $C_6H_6$ , m.p. 179.5–180.5° (239); note that this prod. does not rearrange.]

 $\bar{C}$  with Secondary Amines

With aliphatic *sec.* amines. [ $\bar{C}$  with  $Me_2NH$  in  $C_6H_6$  gives (65% yield (240)) trityl-dimethyl-amine, cryst. from aba. alc., m.p. 95–97° (240), 97° (236).]

With aromatic *sec.* amines. [ $\bar{C}$  with diphenylamine might first be expected to give *N*-trityl-diphenylamine, ndls. from toluene, m.p. 172° (241), which has actually been prepd. by other means (241) (242) (243); however,  $\bar{C}$  with diphenylamine (244) in hot  $C_6H_6$  (243) or pyridine (165) or the above *N*-trityl-diphenylamine with diphenylamine  $HCl$  in  $C_6H_6$  or in hot  $AcOH$  directly (243) gives the rearr. prod., viz., 4-trityl-diphenylamine (4-anilino-tetraphenylmethane), m.p. 242° (243) (244), 240° (165). — For use of these and related prods. as antioxidants see (244) (245). — For analogous behavior of  $\bar{C}$  with di-*p*-tolylamine, di-*p*-amylamine, and di-(*p*-dimethylaminophenyl)amine see (243).]

[For behavior of  $\bar{C}$  with *N,N*-diphenyl-*p*-phenylenediamine yielding a blue meriquinoid salt, m.p. 182–183°, see (246) (247) (248); with indole and with 2-methylindole giving *N*-trityl derivs. see (196).]

With heterocyclic *sec.* amines. [ $\bar{C}$  with piperidine in  $C_6H_6$  yields (179) *N*-tritylpiperidine, ndls. from alc., m.p. 153° (179).]

 $\bar{C}$  with Tertiary Amines

With aliphatic *ter*-amines. [ $\bar{C}$  with  $Me_3N$  in acetonitrile +  $CHCl_3$  at room temp. ppts. a prod., m.p. 190–195° dec. (249), of compn.  $2(C_6H_5)_3COH \cdot (CH_3)_3N \cdot HCl$  from which extraction with aq. leaves triphenylcarbinol (1:5985), m.p. 161°, or from which extraction with  $C_6H_6$  leaves the trimethylamine  $HCl$ . — For analogous behavior of  $\bar{C}$  with  $Et_3N$  see (249) ]

With aromatic *ter*-amines.  $\bar{C}$  with 3 wts. dimethylaniline at 100–115° for 8 hrs. gives (42% yield (250)) 4-trityldimethylaniline (4-dimethylamino-tetraphenylmethane), cryst. from alc., m.p. 204–205° (250), 208° (251).]

With heterocyclic *ter*-amines.  $\bar{C}$  with pyridine does not give a simple quaternary salt; however,  $\bar{C}$  with pyridine in nitromethane +  $CHCl_3$  (249) or in EtOAc (249), or  $\bar{C}$  in dry pyridine with exactly 1 mole  $H_2O$  (84) (252) (165), gives a definite prod., cryst. from acetone (249) or  $CHCl_3$  (42), m.p. 176° (42), 174° (34) (253) (165), 172–174° (84), 170–175° (249); this prod. is formulated as ether  $(C_6H_5)_3C.OH \cdot C_5H_5N.HCl$  (249) or as  $(C_6H_5)_3CCl \cdot C_5H_5N.H_2O$  (84) (252) (42).]

#### BEHAVIOR OF $\bar{C}$ WITH ARYLHYDRAZINES

With monoaryldiazines.  $\bar{C}$  with phenylhydrazine (2 moles) in dry ether at room temp. gives (90% yield (254)) *N*-trityl-*N*-phenylhydrazine [Beil. XV-581, XVI-(184)], cryst. from boilg. abs. alc., m.p. 136–137° (254), 148° (255). [Note that this prod. is easily oxidized (dehydrogenated), e.g. with nitrous oxides (100% yield (254), 86% (256)) or  $Br_2/aq.$  (100% yield (257)) giving tritylazobenzene  $(C_6H_5)_3C-N=N-C_6H_5$  [Beil. XVI-85], m.p. 113–114° (254), 110° (255), 110–112° (256) (for study of thermal decompn. of this prod. see (258)).]

$\bar{C}$  with *p*-nitrophenylhydrazine in a large vol.  $C_6H_6$  gives (257) cf. (256) *N*-trityl-*N*-(*p*-nitrophenyl)hydrazine, m.p. 170° (250).]

With diaryldiazines.  $\bar{C}$  with *N,N*-(unsym.)-diphenylhydrazine (2 moles) in  $C_6H_6$  refluxed 20 min. gives (259) *N'*-trityl-*N,N*-diphenylhydrazine, m.p. 136–137° (259). —  $\bar{C}$  with *N,N'*-diphenylhydrazine (hydrazobenzene) (2 moles) in dry ether under  $CO_2$  refluxed 16 hrs. gives (259) *N'*-trityl-*N,N*-diphenylhydrazine, m.p. 107° (259) (in this connection recall also that  $\bar{C}$  with hydrazobenzene in boilg.  $C_6H_6$  is in part reduced (79) to triphenylmethane)]

#### BEHAVIOR OF $\bar{C}$ WITH AMIDES

$\bar{C}$  (2 moles) with urea (1 mole) in dry pyridine at 100° gives (165) cf. (179) *N,N'*-ditritylurea, cryst. from alc. with 2 EtOH not lost on air drying, m.p. 245° (165); note that *N*-tritylurea (prepd. indirectly (124)) has m.p. 234–235° dec. (124). —  $\bar{C}$  (1 mole) + thiourea in pyridine at 100° for 1 hr. gives (165) cf. (179) *N*-tritylthiourea, cryst. from  $C_6H_6$ , m.p. 222° dec. (165), 217° (179).]

#### BEHAVIOR OF $\bar{C}$ WITH HYDRAZIDES

$\bar{C}$  with free semicarbazide ( $NH_2CONH.NH_2$ ) in pyridine at 0° gives (88% yield (260)) 1-tritylsemicarbazide, cryst. from abs. alc. with 1 EtOH, m.p. 186–188° dec.; the solvate alc. is lost in vac. at 110° after 6 hrs. and m.p. rises to 190–192° (260).]

$\bar{C}$  with primary hydrazides (acylhydrazine) in general reacts to give *N*-trityl-*N*-acylhydrazines which upon suitable dehydrogenation give *N*-trityl-*N*-acyl-azo compounds; the topic cannot here be expanded but for many examples see (260) (261).]

① Triphenylmethane (1:7220): lfts. from alc. [From  $\bar{C}$  in anhydrous formic acid (1:1005) at 100° for 2 hrs. in 90% yield (4).]

② Triphenylcarbinol (1:5985): cryst. from  $C_6H_6$  or alc., m.p. 161–162°. [From  $\bar{C}$  on boilg. with aq.]

③ Trityl methyl ether: cryst. from MeOH, m.p. 82–83°. (See text above under behavior of  $\bar{C}$  with alcohols.)

④ Trityl ethyl ether: cryst. from EtOH, m.p. 83–84°. (See text above under behavior of  $\bar{C}$  with alcohols.)

© *N*-Tritylphthalimide: tbls. from alc., m.p. 172° (179). [From  $\bar{C}$  with K phthalimide at 200° (179).]

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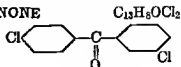
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### 3:3415 3,4'-DICHLOROBENZOPHENONE

(*m*-Chlorophenyl *p*-chlorophenyl ketone)



Beil. S.N. 652

M.P. 112.6-113.4° (1)

[For prepn. of  $\bar{C}$  from 1,1-dichloro-2-(*m*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene (3:9863) by oxidn. with  $CrO_3$  (41% yield) see (1).]

① 3,4'-Dichlorobenzophenone 2,4-dinitrophenylhydrazone: m.p. 258-260° (1).

3:3415 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* 67, 1601-1602 (1945).

## 3:3420 5,8-DICHLORONAPHTHOL-1

 $C_{10}H_6OCl_2$ 

Beil. VI-613

VI<sub>1</sub>—VI<sub>2</sub>—

M.P. 114–115° (1)

Cryst. (from CS<sub>2</sub>) (1). — Spar. sol. hot aq. (1).

[For prepn. (in very poor yield) from  $\gamma$ -(2,5-dichlorophenyl)paraconic ac. [Beil. XVIII-422] by distn. see (1)]

$\bar{C}$  with FeCl<sub>3</sub> gives a white turbidity, changing on warming to flocculent violet ppt. (1).

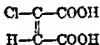
$\bar{C}$  in alk. soln. coupled with diazotized naphthionic acid (1-naphthylaminesulfonic acid-4) gives dark violet color (1).

[For use in dyestuff industry see (2) (3) (4).]

⑤ 5,8-Dichloro-1-naphthyl acetate: yellowish pr. from CS<sub>2</sub> + lgr., m.p. 144–145° (1).

3:3420 (1) Erdmann, Schwechten, *Ann* 275, 285 (1893). (2) Aktien Ges. für Anilin Fabrikation, French 517,558, May 7, 1921; *Cent.* 1921, IV 194. (3) Soc. Chem. Ind. Basel, French 593,751, Aug. 31, 1925, *Cent.* 1926, I 1048. (4) Soc. Chem. Ind. Basel, Swiss 185,148, Sept. 16, 1936; *Cent.* 1937, I 1561.

## 3:3432 CHLOROMALEIC ACID

 $C_4H_3O_4Cl$ 

Beil. II-752

II<sub>1</sub>—II<sub>2</sub>-(G46)

M.P. 115° (1) (2)

114–115° (3) (4)

[108° after sintering at 95° (5) (6)]

[See also chlorofumaric acid (3:4853).]

Cryst. from AcOH/CHCl<sub>3</sub>, ether/CHCl<sub>3</sub>, ether/pet. ether, or ether alone. — Eas. sol. alc, ether, AcOH; spar. sol. CHCl<sub>3</sub> or C<sub>6</sub>H<sub>6</sub>; insol. pet. ether.

[For prepn. of  $\bar{C}$  from *meso*- $\alpha,\alpha'$ -dichlorosuccinic acid (3:4930) with NaOAc/dil. AcOH on boilg. (5) (1), or from its neutral sodium salt in aq. soln. on boilg.  $\frac{1}{2}$  hr. (4), see indic. refs.; from chloromaleic anhydride (3:0280) by hydrolysis with aq. and subsequent evapn. see (4) (5) (6) (7); from 3,5,5,5-tetrachloro-4-ketopenten-2-oic acid-1 ("  $\beta$ -(trichloroacetyl)- $\beta$ -chloroacrylic acid ") [Beil. III-733] on 24 hr. stdg. at room temp. of its soln. in excess 10% aq. Na<sub>2</sub>CO<sub>3</sub> see (6); from chloromaleonitrile (b.p. 185° at 753 mm., 71.0–71.5° at 10 mm.,  $D_4^{20} = 1.2293$ ,  $n_D^{20} = 1.48944$  (9)) by hydrol. see (9).]

$\bar{C}$  on htg. at 180° loses H<sub>2</sub>O yielding (6) chloromaleic anhydride (3:0280).

$\bar{C}$  although unchanged by conc. HCl at ord. temp. for as long as 10 days (4) is by repeated evapn. with conc. HCl (7) isomerized to chlorofumaric acid (3:4853).

$\bar{C}$  in aq. soln. with Zn filings is dehalogenated yielding (4) fumaric acid (1:0895);  $\bar{C}$  (as Na<sub>2</sub>X) in aq. soln. with 1% Na/Hg gives (4) mainly succinic acid (1:0530) accompanied by some fumaric acid (1:0895).

$\bar{C}$  readily reduces aq. KMnO<sub>4</sub>.

[ $\bar{C}$  readily combines with Br<sub>2</sub> if heated in s.t. to 100° (7).]

$\bar{C}$  behaves normally as a dibasic acid: e.g., titration with standard dil. aq. alk. gives Neut. Eq. 75.3; for study of electrometric titration see (1).

[Salts: KH<sub>2</sub>A, eas. sol. aq. (dif. from corresp. salt of chlorofumaric acid (3:4853)), e.g., 100 g. of its satd. aq. soln. at 15° cont. 29.2 g. of KH<sub>2</sub>A (7); for crystallographic data see (7).]



—  $\text{NaH}\bar{\text{A}}\cdot 3\text{H}_2\text{O}$ , eas. sol. aq. (7). —  $\text{Ag}_2\bar{\text{A}}$ , insol. aq. (7). —  $\text{Ba}\bar{\text{A}}\cdot 2\text{H}_2\text{O}$  (4) (5) (6), spar. sol. aq. —  $\text{Ca}\bar{\text{A}}\cdot 4\text{H}_2\text{O}$  (4). —  $\text{Sr}\bar{\text{A}}\cdot 4\frac{1}{2}\text{H}_2\text{O}$ , spar. sol. cold aq. (5). —  $\text{Ph}\bar{\text{A}}$ , insol. aq. (4).]

[ $\bar{\text{C}}$  on stdg. at ord. temp. with slight excess 0.76 *N* aq. KOH gives chlorine ion only  $\frac{1}{40}$  as rapidly (4) as the isomeric chlorofumaric acid (3:4853).]

The acid chloride corresp. to  $\bar{\text{C}}$ , viz., chloromaleyl (di)chloride (3:6158) q.v., has been reported only by indirect means.

— Dimethyl chloromaleate: oil (see 3:9351).

— Diethyl chloromaleate: oil (see 3:6697).

⑧ Chloromaleanil [*N*-phenyl-chloromaleimide]: ndls. from hoilg. alc., m.p. 170° (8). [From aniline salt of  $\bar{\text{C}}$  (or of chlorofumaric acid) on htg. for a few minutes at 170–180° (8); note that this prod. on htg. with aniline yields (8)  $\alpha$ -anilinosuccinanil [Beil. XXI-554, XXI-432]], yel. cryst. from acetone +  $\text{C}_6\text{H}_6$ , m.p. 232° (8), and that a little of this latter cpd. which may accompany the former is readily removed from it by washing with warm  $\text{C}_6\text{H}_6$  (8).]

⑨ Chloromaleic *p*-chloroanil [*N*-(*p*-chlorophenyl)chloromaleimide]: pl. from hot alc., m.p. 175° (8). [From *p*-chloroaniline salt of  $\bar{\text{C}}$  on htg. for a few minutes at 170–180° (8).]

⑩ Chloromaleic *p*-bromoanil [*N*-(*p*-bromophenyl)chloromaleimide]: microcrystn. powder from hoilg. alc., m.p. 190° (8). [From *p*-bromoaniline salt of  $\bar{\text{C}}$  on htg. for a few minutes at 170–180° (8).]

(2) Stelling, *Z. physik.* 11, 4 (1925). (4) Michael, *ler Riet, Ann.* 280, 224-225. (5) *Chem. Soc.* 53, 706-708 (1925). (6) Mommaerts, *Bull. classe sci., Acad. roy. Belg.* (2), 1925, 33, 3621 (1944).

### 3:3445 2,7-DICHLORONAPHTHALENE



$\text{C}_{10}\text{H}_8\text{Cl}_2$  Beil. V - 544

$V_1$ —

$V_2$ -(446)

M.P. 115° (10)

114–115° u.c. (1)

114° (2) (3)

Cryst. from alc. or  $\text{C}_6\text{H}_6$ ; sublimes under reduced press. — Eas. sol. hoilg. alc.

[For prepn. of  $\bar{\text{C}}$  from naphthalene-2,7-bis-(sulfonyl chloride) [Beil. XI-217] (4) (1), from 7-chloronaphthalene-2-sulfonyl chloride [Beil. XI-181] (4) (5), from 7-bromonaphthalene-2-sulfonyl chloride [Beil. XI-184] (7), from sodium 7-hydroxynaphthalenesulfonate-2 [Beil. XI-285, XI-1-67] (3) by htg. with  $\text{PCl}_5$  as directed, see indic. refs.; from 7-sulfonaphthylamine-2 [Beil. XIV-763, XIV-1-736] by treatment of the corresp. diazonium chloride with  $\text{PCl}_5$  in  $\text{POCl}_3$  see (8); from 3,6-dichloronaphthalimide or 3,6-dichloronaphthalic acid (3:4870) with  $\text{HgO}$  + aq. in a.t. 6 hrs. at 200–210° see (10)]

$\bar{\text{C}}$  on oxidn. with dil.  $\text{HNO}_3$  ( $D = 1.21$ ) in a.t. at 140° yields (9) 4-chlorophthalic acid (3:4390), m.p. 157°.

[ $\bar{\text{C}}$  on mononitration yields (9) a prod., m.p. 141.5–142°.]

[ $\bar{\text{C}}$  on treatment with chlorosulfonic acid in  $\text{CS}_2$ , followed by conversion as directed (11), yields mixt. of two sulfonic acids; the major prod. is 2,7-dichloronaphthalenesulfonic acid-3 (corresp. sulfonyl chloride, m.p. 166°, corresp. sulfonamide, m.p. 218° (12)), the minor prod. (10% of total) is 2,7-dichloronaphthalenesulfonic acid-4 (corresp. sulfonyl chloride, m.p. 152°) (11)]

# CHAPTER IX

## VISION A. SOLIDS

(3:3500-3:3999)

-2



$C_{10}H_7OCl$

Beil. VI - 649

VI<sub>1</sub>—

VI<sub>2</sub>-(603)

., ether, AcOH,  $C_6H_6$ ,  $CHCl_3$ ,  $CS_2$  — Sublimes in naphthol-2 (3:2965), m.p.  $101^\circ$  to  $79-88^\circ$  (2).

phthol-2 (3:3600) with  $FeSO_4 + NaOH$  see (4);  
'2) (3) with Na/Hg in dil. HCl see (2) (3); from K  
VI-282, XI<sub>1</sub>-(66)] with 3 moles  $PCl_5$  at  $165^\circ$  as

press and at elevated temp. yields (5) 6-chloro-  
AcOH, m.p.  $260^\circ$  (5) ]

) in s.t. at  $190-200^\circ$  gives (6) 4-chlorophthalic

$14-125^\circ$  (3).

ndls. from much alc., m.p.  $146-147^\circ$  (2).  
and shaken with m-nitrobenzoyl chloride (2).]

5 (100%) 101 D. 1.3615 (20) n<sub>D</sub> 1.5815 (20)  
(5)

$C_8H_5OCl$

Beil. VI —

VI<sub>1</sub>—

VI<sub>2</sub>-(463)

73

inol = sym.-m-xyleneol)

6% yield (2)) or from

(7<sub>2</sub> or  $SO_2Cl_2$  (5) see

7<sub>2</sub> (3:0844

compl

from pentachlorobenzene (3:2290) with  $N/2$  MeOH/NaOMe at  $180^\circ$  in s.t. for  $7\frac{1}{2}$  hrs. (note that some of the isomeric 2,3,4,5-tetrachlorophenol (3:3523) is also formed) see (1).]

$\bar{C}$  in aq. behaves as a fairly strong acid,  $K$  at  $25^\circ = 3.3 \times 10^{-6}$  (2), and can be directly titrated with  $N/10$  aq. NaOH (3) (1), Neut. Eq. = 232.

$\bar{C}$  (1 wt. pt.) added to  $HNO_3$  ( $D = 1.5$ , 6 wt. pts.) in 20 pts. AcOH at  $10^\circ$ , and after 1 hr. poured onto ice, gives (65% yield (4)), 2,3,5,6-tetrachloro-4-nitrophenol, ndls. from AcOH, m.p.  $148-149^\circ$  dec. (4) (corresp. acetate, ndls. from dil. alc., m.p.  $113-114^\circ$  (4)).

② 2,3,5,6-Tetrachlorophenol methyl ether (2,3,5,6-tetrachloroanisole): ndls. from alc., m.p.  $88^\circ$  (1). [From  $\bar{C}$  with alk. +  $Me_2SO_4$  (1).] — [Note that this prod. on nitration with 4-5 wt. pts.  $HNO_3$  ( $D = 1.5$ ) at  $0^\circ$  gives (95% yield (4)) 2,3,5,6-tetrachloro-4-nitroanisole, ndls. from dil. alc., m.p.  $112-113^\circ$  (4).]

— 2,3,5,6-Tetrachlorophenol ethyl ether (2,3,5,6-tetrachlorophenetole): m.p.  $56^\circ$  (5). [Reported by indirect means (5).]

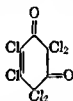
— 2,3,5,6-Tetrachlorophenyl acetate: unreported.

③ 2,3,5,6-Tetrachlorophenyl benzoate: m.p.  $136^\circ$  (5). [From  $\bar{C}$  + large excess BzCl in aq. alk. (5).]

— 2,3,5,6-Tetrachlorophenyl *N*-phenyl carbamate: unreported.

3:3460 (1) Holleman, van der Hoeven, *Rec. trav. chim.* **39**, 746-748 (1920). (2) Tiessens, *Rec. trav. chim.* **48**, 1063 (1929). (3) Tiessens, *Rec. trav. chim.* **50**, 116, 119 (1931). (4) Peters, Rowe, Stead, *J. Chem. Soc.* 1943, 233-235. (5) Bures, Kovarovicova, *Časopis Českoslov. Lékařnictva* **10**, 197-202, 233-239 (1930); *Cent.* 1930, II 2775; *C.A.* **25**, 1816-1817 (1931).

3:3470 1,2,4,4,6,6-HEXACHLORO-  
CYCLOHEXEN-1-DIONE-3,5  
("Hexachlororesorcinol")



$C_6O_2Cl_6$

Beil. VII - 572  
VII<sub>1</sub>—

M.P.  $115^\circ$  (1) B.P.  $159-160^\circ$  at 13-15 mm. (1)

Colorless tbs. or thick pr. (from AcOH or ether/pet. ether). — Penetrating lachrymatory odor. —  $\bar{C}$  can be distd. at atm. press. without decompn. — Eas. sol. ether,  $CHCl_3$ ,  $C_6H_6$ ; spar. sol. pet. ether. — Readily forms supersatd. solns.

[ $\bar{C}$  is formed from pentachlorobenzoic acid (Beil. VI, 404) by actn. of  $Cl_2$  in AcOH see (1)]  
 $\bar{C}$  AcOH reduces smoothly (1) to tetra

[For use as seed disinfectant see (2); for other reactions see (1).]

3:3470 (1) Zinke, Fuchs, *Ber.* **24**, 2689-2690 (1892). (2) Bonrath, Urbach (to I.G.), *Ger.* 534,597, Sept. 29, 1931, *Cent.* 1931, II 3143.

# CHAPTER IX

## DIVISION A. SOLIDS

(3:3500-3:3999)

3:3500 6-CHLORONAPHTHOL-2



$C_{10}H_7OCl$

Beil. VI - 649

VI<sub>1</sub>—

VI<sub>2</sub>-(603)

M.P. 115° (1) (2) (3) (4)

Ndls. from hot aq. (1) (2); sol. alc., ether, AcOH,  $C_6H_6$ ,  $CHCl_3$ ,  $CS_2$ . — Sublimes in prisms. —  $\bar{C}$  depresses m.p. of 8-chloronaphthol-2 (3:2965), m.p. 101° to 79–88° (2).

[For prepn of  $\bar{C}$  from 1,6-dichloronaphthol-2 (3:3600) with  $FeSO_4 + NaOH$  see (4); from 6-chloronaphthol-2-sulfonic acid-4 (2) (3) with  $Na/Hg$  in dil.  $HCl$  see (2) (3); from K salt of 2-naphtholsulfonic acid-6 [Beil. XI-282, XI<sub>1</sub>-(66)] with 3 moles  $PCl_5$  at 165° as directed see (1) (2).]

( $\bar{C}$  as dry sodium salt) with  $CO_2$  under press. and at elevated temp yields (5) 6-chloro-2-hydroxynaphthoic acid-3, yel. lfts. from AcOH, m.p. 260° (5).]

$\bar{C}$  on oxida. with dil.  $HNO_3$  ( $D = 1.13$ ) in s.t. at 190–200° gives (6) 4-chlorophthalic acid (3:4390).

① 6-Chloro-2-naphthyl benzoate: m.p. 124–125° (3).

② 6-Chloro-2-naphthyl *m*-nitrobenzoate: ndls from much alc., m.p. 146–147° (2).

[From  $\bar{C}$  dislvd. in 10%  $NaOH$  at 50–60° and shaken with *m*-nitrobenzoyl chloride (2).]

3:3500 (1) Claus, Zimmermann, *Ber.* 14, 1483–1485 (1881). (2) Ruggli, Knapp, Merz, Zimmermann, *Helv. Chim. Acta* 12, 1048–1050 (1929). (3) Battagay, Silbermann, Kienzie, *Bull. soc. chim.* (4) 49, 721 (1931). (4) Herzberg, Spengler, Schmid (to I.G.), *Ger.* 431,165, June 30, 1926; *Cent.* 1920, II 1196 (5) Lange, Luce, Jacobs (to I.G.), *Ger.* 564,128, Nov. 14, 1932; *Cent.* 1933, II 446. (6) Claus, Dehne, *Ber.* 15, 321 (1882).

3:3505 4-CHLORO-3,5-DIMETHYLPHENOL  
(2-Chloro-*m*-5-xyleneol)



$C_8H_7OCl$

Beil. VI —

VI<sub>1</sub>—

VI<sub>2</sub>-(463)

M.P. 115–116° (1)

B.P. 246° (2)

115° (3) (4)

114–115° (2)

Cryst. from benzene.

[For prepn of  $\bar{C}$  from 3,5-dimethylphenol (*m*-5-xyleneol = *sym*-*m*-xyleneol) (1:1455) with  $SO_2Cl_2$  (1 mole) in  $CHCl_3$  (1) or with  $Cl_2$  in AcOH (66% yield (2)) or from crude coal-tar fraction consisting mainly of 3,5-dimethylphenol with  $Cl_2$  or  $SO_2Cl_2$  (5) see indic. refs. (note that some 2-chloro-3,5-dimethylphenol (6-chloro-*m*-5-xyleneol) (3:0844) is formed as a by-product (1) (5); also that 3,5-dimethylphenol in AcOH on complete saturation

[Note that, in addition to its ordinary use to designate  $\bar{C}$  specifically, the term "chloralide" is also used generically to denote a class of compounds formed by condensation of chloral (3:5210) with  $\alpha$ -hydroxy acids.]

Cryst. from alc. or ether; eas. sublimable; insol. aq.; eas. sol. hot but spar. sol. cold alc.; eas. sol. ether; cas. sol. in 80% AcOH (dif. and sepn. from metachloral (1)). — For crystallographic studies see (10).

Note that m.p. of  $\bar{C}$  is almost identical with that of  $\alpha$ -parachloral, m.p. 116°, but that mixed m.p. of the two is depressed as low as 85–90° (2);  $\beta$ -parachloral, however, has m.p. 152° (2).

[For prepn. of  $\bar{C}$  from chloral (3:5210) or chloral hydrate (3:1270) with conc. or fuming  $H_2SO_4$  (yields: 61% (11), 44–51% (4) both based on chloral hydrate) see (11) (4) (8) (12) (6); for formn. of  $\bar{C}$  from chloral hydrate with  $H_2SO_4$  as a by-product (abt. 2% (2)) in prepn. of  $\alpha$ - and  $\beta$ -parachloral + metachloral, or from chloral by warming with  $AlCl_3$  (1), see indic. refs.; for formn. of  $\bar{C}$  from chloral with  $ClSO_3H$  as by-prod. of prepa. of octachlorodiethyl ether (3:0738) see (3); for formn. of  $\bar{C}$  from chloral (excess) with  $\beta,\beta$ -trichloro- $\alpha$ -hydroxypropionic acid (trichlorolactic acid) [Beil. III-286, III<sub>1</sub>-(111), III<sub>2</sub>-(210)] in s.t. at 150–160° see (4) (13) cf. (17).]

[ $\bar{C}$  on reduction with Zn + HCl in alc. soln. gives according to conditions very small amts. of  $\beta,\beta$ -dichloroacrylic acid (3:1875) (14) (15) (16),  $\beta$ -chloroacrylic acid (3:2240) (11), and acetaldehyde (1:0100) (15) (16).] — [ $\bar{C}$  is unaffected by boilg.  $HNO_3$  (8).]

[ $\bar{C}$  with  $PCl_5$  in s.t. at 270–290° for several days gives (18) (9) 5-chloro-2,5-bis-(trichloromethyl)dioxolane-1,3-dio-4 ("trichlorolactic acid-tetrachloroethylidene ether-ester") [Beil. XIX-105], oil, b.p. 276° (18),  $D_4^{20} = 1.7426$  (18).]

$\bar{C}$  with boilg. alkalis undergoes hydrolytic cleavage yielding (4) (12) (6) (7) chloroform (3:5050) and salts of formic acid (1:1005).

[ $\bar{C}$  with abs. EtOH in s.t. at 140–150° gives (16) (4) chloral ethylalcoholate (3:0860) and ethyl  $\beta,\beta,\beta$ -trichlorolactate [Beil. III-287, III<sub>1</sub>-(111), III<sub>2</sub>-(210)], m.p. 66–67°.]

3:3510 (1) Böeseken, *Rec. trav. chim.* 29, 108 (1910). (2) Chattaway, Kellett, *J. Chem. Soc.* 1928, 2709–2712. (3) Fuchs, Katscher, *Ber.* 62, 2384–2385 (1929). (4) Wallach, *Ann.* 193, 4, 8, 11–19 (1878). (5) Wallach, *Ber.* 6, 118, Note (1873). (6) Städel, *Ann.* 61, 104–114 (1847); 106, 253–255 (1858). (7) Personne, *Bull. soc. chim.* (2) 21, 520 (1874). (8) Grabowski, *Ber.* 8, 1433–1437 (1875). (9) Anschütz, Haslam, *Ann.* 239, 297–300 (1887). (10) Wallach, Bodewig, *Ann.* 193, 58–59 (1878); *Z. Krist.* 1, 594 (1877).

(11) Otto, *Ann.* 239, 262–266 (1887). (12) Kekulé, *Ann.* 105, 293–295 (1858). (13) Wallach, Heymer, *Ber.* 9, 545–547 (1876). (14) Wallach, *Ann.* 203, 83–84 (1880). (15) Wallach, *Ann.* 193, 6, 20, 27 (1878). (16) Wallach, *Ber.* 8, 1578–1583 (1875). (17) Routala, Neovius, *Ber.* 57, 252, Note 4 (1924). (18) Anschütz, Haslam, *Ann.* 253, 121–123 (1889).

3:3520 2,4,6-TRICHLORO-3-HYDROXYBENZALDEHYDE



$C_7H_3O_2Cl_3$

Beil. VIII-61  
VIII<sub>1</sub>—

M.P. 115.5–116.5° (1)  
115–116° (6)  
114° (2)  
113° (3)

Colorless cryst. from 50% AcOH;  $\bar{C}$  seps. with AcOH of crystn. but this immediately effervesces in air. —  $\bar{C}$  has pronounced sternutatory props. and on moist skin produces painful blisters (2).

[For prepn. of  $\bar{C}$  from *m*-hydroxybenzaldehyde (1:0055) in AcOH with excess  $Cl_2$  see (1) (2).]

[For condens. of  $\bar{C}$  with 2,4-dichlorophenol (3:0560) see (4), with 2,4-dihydroxybenzoic acid (1:0843) and use of prod. as dye intermediate see (5).]

$\bar{C}$  in 50% aq. KOH warmed for 4 hrs. at 60-70° gives (89.9% yield (3)) 2,4,6-trichlorophenol (3:1573).

$Na\bar{A}$ , pure yel. ndls., spar. sol. aq (2).

$\bar{C}$  in  $Na_2CO_3$  soln. with  $Me_2SO_4$  yields 2,4,6-trichloro-3-methoxybenzaldehyde, ndls. from alc., m.p. 76° (2); on very slow oxidn. with alk.  $KMnO_4$ , this prod. yields 2,4,6-trichloro-3-methoxybenzoic acid, m.p. 109° (2)

② 2,4,6-Trichloro-3-hydroxybenzaldehyde: ndls. from dil. alc., m.p. 174° (2), 170° (6). [This with boilg.  $Ac_2O$  yields 2,4,6-trichloro-3-acetoxybenzonitrile, lfts. from dil. AcOH, m.p. 82-83° (6).]

③ 2,4,6-Trichloro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazone: yel.-or. ndls., m.p. 272-273° dec (2) [From  $\bar{C}$  in alc. with *p*-nitrophenylhydrazine + 1 drop aq. (2).]

3:3520 (1) Bissell, Kranz (to Nat. Aniline & Chem. Co.), US 1,770,803, Sept. 30, 1930; *Cent.* 1931, I 159; *C.A.* 24, 5769 (1930). (2) Hodgson, Beard, *J. Chem. Soc.* 1926, 148-149, 153. (3) Lock, *Monatsh.* 55, 312 (1930). (4) I.G., Swiss 137,923-137,929, incl., 138,160-138,163, incl., April 16, 1930, *Cent.* 1930, II 1453. (5) Weiter (to F. Bayer & Co.), U.S. 1,532,790, April 7, 1925; *Cent.* 1925, II 352. (6) Krause, *Ber.* 32, 123 (1899).

### 3:3523 2,3,4,5-TETRACHLOROPHENOL



$C_6H_2OCl_4$  Beil. S.N. 522

M.P. 116-117° (1)

116° (2) (3)

[For prepn. of  $\bar{C}$  from 2,3,4,5-tetrachloroaniline [Beil. XII-630, XII<sub>1</sub>-(313)] via diazotization and reaction with aq. (65% yield) see (1); from 2-amino-3,4,5,6-tetrachlorophenol [Beil. XII-386] (3) via diazotization and elimination of diazo group with alc. see (3); for formn. of  $\bar{C}$  from pentachlorobenzene (3:2290) with *N*/2 MeOH/ $NaOMe$  at 180° in s.t. for 7½ hrs. as by-prod. of the isomeric 2,3,5,6-tetrachlorophenol (3:3460) see (4).]

$\bar{C}$  in aq. behaves as an acid,  $K_{nt} 25^\circ = 1.1 \times 10^{-7}$ , and can be titrated with *N*/10 aq. NaOH (1), Neut. Eq. = 232.

— 2,3,4,5-Tetrachlorophenol methyl ether (2,3,4,5-tetrachloroanisole): m.p. 83° (3). [Reported only by indirect means (4).]

— 2,3,4,5-Tetrachlorophenol ethyl ether (2,3,4,5-tetrachlorophenetole): unreported.

— 2,3,4,5-Tetrachlorophenyl acetate: unreported.

③ 2,3,4,5-Tetrachlorophenyl benzoate: m.p. 110° (4) (5). [Note that this prod. depresses m.p. of corresp. benzoate from the isomeric 2,3,4,6-tetrachlorophenol (3:1687) (5).]

— 2,3,4,5-Tetrachlorophenyl *N*-phenylcarbamate: unreported.

3:3523 (1) Tiessens, *Rec. trav. chim.* 50, 115-110, 119 (1931). (2) Tiessens, *Rec. trav. chim.* 49, 1068 (1929). (3) Bures, Haslinova, *Časopis Českoslov. Lékárnicka*, 9, 101-107, 129-134, 153-157 (1929); *Cent.* 1929, II 1403; *C.A.* 24, 2998 (1930). (4) Holleman, van der Hoeven, *Rec. trav. chim.* 39, 745 (1920). (5) Holleman, *Rec. trav. chim.* 40, 318-319 (1921).

3:3525 4,5-DICHLOROCATECHOL  
(4,5-Dichloropyrocatechol)



$C_6H_4O_2Cl_2$  Beil. VI - 783  
VI<sub>1</sub>-(389)  
VI<sub>2</sub>—

M.P. 116-117° (1)  
105-106° (2) (3)  
(See text)

Colorless pr. from  $CHCl_3 + CS_2$  (1); ndls. from  $C_6H_6 +$  pet. ether (2). —  $\bar{C}$  is eas. sol. in cold aq. from which it crystallizes as a hemihydrate (1) (it is possible that the m.p. of 105-106° observed by some workers may have been due to formn. of this prod.). —  $\bar{C}$  cryst. from AcOH with 1 mole of solvent, viz.,  $\bar{C} \cdot AcOH$  (1).

[For prepn. of  $\bar{C}$  from pyrocatechol (1:520) with  $SO_2Cl_2$  (2 moles) or from 4-chloropyrocatechol (3:2470) with  $SO_2Cl_2$  (1 mole) see (2).]

[ $\bar{C}$  with silver oxide in dry ether gives (1) 4,5-dichlorobenzoquinone-1,2 [Beil. VII<sub>1</sub>-(338)], m.p. 94°; note, however, that  $\bar{C}$  with this prod. forms a corresp. quinhydrone, dec. abt. 85°.]

[ $\bar{C}$  with  $Cl_2$  in AcOH gives (1) 3,4,5-trichloropyrocatechol (3:3448) cryst. from aq. as monohydrate, m.p. abt. 106-109° (1), 104-105° (4), 115° (5).]

[ $\bar{C}$  with  $PCl_5$  gives (2) 1,2,4,5-tetrachlorobenzene (3:4115).]

$\bar{C}$  with  $N/10$  aq. KOH titrates (1) as a monobasic acid, i.e., Neut. Eq. = 89.5. —  $\bar{C}$  with aq.  $FeCl_3$  gives blue-green coloration becoming red on addn. of aq.  $Na_2CO_3$  (1).

$\bar{C}$  does not (5) condense with xanthydrol (1:5205) in AcOH (dif. from 4-chloropyrocatechol (3:2470)).

— 4,5-Dichloropyrocatechol diacetate: unreported.

⊙ 4,5-Dichloropyrocatechol dibenzoate [Beil. IX<sub>1</sub>-(72)]; m.p. 140.0-140.5° (1).

— 4,5-Dichloropyrocatechol 1-methyl ether (4,5-dichloroguaiacol) [Beil. VII-783]: ndls. from pet. ether, m.p. 71-72° (7). [Prepd. indirectly (7).]

— 4,5-Dichloropyrocatechol dimethyl ether (4,5-dichloroveratrole) [Beil. VII-783]: ndls. from alc., m.p. 85.5-86.5° (7). [From the preceding monomethyl ether with MeI + aq. KOH (7).]

3:3525 (1) Willstätter, Müller, *Ber.* 44, 2184-2186 (1911). (2) Peratoner, *Gazz. chim. ital.* 28, I 222-224 (1898). (3) Frejka, Seifranek, Zika, *Collection Czechoslov. Chem. Commun.* 9, 243-244 (1937). (4) Cousin, *Bull. soc. chim.* (3) 13, 719 (1895); *Ann. chim.* (7) 13, 483 (1898). (5) Jackson, Boswell, *Am. Chem. J.* 35, 526-527 (1906). (6) Fabre, *Ann. chim.* (9) 18, 115 (1922). (7) Peratoner, Ortoleva, *Gazz. chim. ital.* 28, I, 229-232 (1898).

3:3530 5-CHLORORESORCINOL



$C_6H_5O_2Cl$  Beil. VI —  
VI<sub>1</sub>—  
VI<sub>2</sub>-(819)

M.P. 117° (1)

$\bar{C}$  cryst. from  $C_6H_6$  in colorless ndls. of monohydrate, m.p. 67° (1), which on sublimation in vac. yield anhydrous  $\bar{C}$  (1).

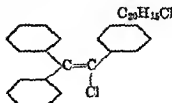
$\bar{C}$  is readily sol. in all usual solvents except lt. pet.; it rapidly absorbs aq. regenerating above monohydrate, m.p. 67° (1).

$\bar{C}$  with  $FeCl_3$  gives bluish-purple color;  $\bar{C}$  reduces hoilg. Fehling soln.

$\bar{C}$  on bromination (no details (1)) yields 5-chloro-2,4-tribromoresorcinol, colorless ndls. from AcOH or dil. alc., m.p. 143° (1).

3:3530 (1) Hodgson, Wignall, *J. Chem. Soc.* 1926, 2827.

**3:3560 1-CHLORO-1,2,2-TRIPHENYLETHYLENE**  
 ("Chlorotriphenylethylene")



Beil. V - 722  
 V<sub>1</sub>-(355)  
 V<sub>1</sub>—

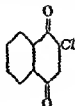
M.P. 117° (1) (2) (3) (4) (5)  
 116-117° (6)

Colorless cryst. from alc. or pet. ether. — Insol. aq.; sol. alc. or lt. pet.; freely sol. ether, acetone, benzene, or  $\text{CHCl}_3$ . — [For use of  $\bar{C}$  in stimulation of action of estrogenic hormones see (7), for aq. susp. of  $\bar{C}$  for medicinal use see (9) ]

[For prepn. of  $\bar{C}$  from 1,1,2-triphenylethanol-1 (benzyl-diphenyl-carbinol) [Beil. VI-721, VI<sub>1</sub>-(354)] in AcOH by treatment with  $\text{Cl}_2$  at 30-40°, then htg. to b.p. to remove AcOH and effect loss of HCl (87% yield), see (1); from 1,2-dichloro-1,1,2-triphenylethane (1) by htg. just above m.p. (115°) (100% yield (1)) or by refluxing 5 hrs. in pyridine (65% yield (1)) see (1); from triphenylethylene [Beil. V-722, V<sub>1</sub>-(355)] in AcOH with  $\text{Cl}_2$  (1), in  $\text{C}_6\text{H}_6$  with  $\text{PCl}_5$  (4), or in  $\text{CCl}_4$  with  $\text{SO}_2\text{Cl}_2$  in pres. of dibenzoyl peroxide (2) see indic. refs.; from  $\omega,\omega$ -diphenylacetophenone (1,1,2-triphenylethanone) (triphenylvinyl alcohol) [Beil. VII-522, VII<sub>1</sub>-(291)] (5) (3) or from triphenylacetaldehyde [Beil. VII<sub>1</sub>-(292)] (6) with  $\text{PCl}_5$  see indic. refs.]

3:3560 (1) van de Kamp, Slettinger, *J. Am. Chem. Soc.* 63, 1876-1881 (1941). (2) Tadros, *Nature* 148, 53 (1941). (3) Schönberg, Robson, Tadros, Fahim, *J. Chem. Soc.* 1949, 1328. (4) Bergmann, Bondi, *Ber.* 64, 1467-1468 (1931). (5) Gardeur, *Bull. acad. roy. Belg.* 34, 67-109 (1897), *Cent.* 1897, II 662. (6) Danilov, *J. Russ. Phys.-Chem. Soc.* 51, 125 (1919); *Cent.* 1923, III 761. (7) Robson, Schönberg, Fahim, *Nature* 142, 292 (1938). (8) MacPherson, Robertson, *Lancet* (2) 237, 1362 (1939). (9) Collie & Imperial Chem. Ind., Ltd., Brit. 543,897, March 18, 1932, *C.A.* 36, 6313 (1942).

**3:3580 2-CHLORONAPHTHO-QUINONE-1,4**  
 (2-Chloro- $\alpha$ -naphthoquinone)



$\text{C}_{10}\text{H}_7\text{O}_2\text{Cl}$  Beil. VII - 729  
 VII<sub>1</sub>—

M.P. 118° (1)  
 117° (2) (3) (4)  
 116-117° (5)  
 116° (9)  
 115° (8)  
 112° u.c. (6)  
 111° (7)

Yel. ndls with pungent quinone odor from dil. alc. or dil. AcOH. — Volatile with steam. — Eas. sol. alc.,  $\text{C}_6\text{H}_6$ ; spar. sol. ether.

[For prepn. of  $\bar{C}$  from naphthoquinone-1,4 ( $\alpha$ -naphthoquinone) (1:9040) by conversion with  $\text{Cl}_2$  in AcOH to 2,3-dichloro-1,4-diketo-1,2,3,4-tetrahydronaphthalene ("  $\alpha$ -naphtho-



quinone dichloride") [Beil. VII-702] and subsequent elimination of 1 HCl with NaOAc/AcOH see (4) cf. (7); from  $\alpha$ -naphthol (1:1500) by conversion with Cl<sub>2</sub> in AcOH to 2,2,4-trichloro-1-keto-1,2-dihydronaphthalene [Beil. VII-387] and subsequent hydrolysis (with rearr.) in boilg. dil. alc. or dil. AcOH see (5).]

[For prepn. of  $\bar{C}$  from 1,3-dichloronaphthalene (3:1310) by oxidn. with CrO<sub>3</sub>/AcOH see (8); from 2,4-dichloronaphthol-1 (3:3250) by oxidn. with CrO<sub>3</sub>/AcOH or HNO<sub>3</sub>/AcOH see (5) (9); from 2-chloro-1,2-diaminonaphthalene (2-chloronaphthylenediamine-1,2) by oxidn. with 2% alk. KMnO<sub>4</sub> see (2); from 2-chloronaphthol-1-sulfonic acid-4 by oxidn. with MnO<sub>2</sub> in boilg. 50% H<sub>2</sub>SO<sub>4</sub> see (1); from 2,4-dinitronaphthol [Beil. VI-617, VI<sub>1</sub>-(308)] by oxidn. with NaOCl in HCl soln. (3) or HCl + KClO<sub>3</sub> (10) see indic. refs.; from sodium salt of 4-(*p*-sulfohenzeneazo)naphthol-1 ("Orange I") [Beil. XVI-275, XVI<sub>1</sub>-(296)] by oxidn. with NaOCl in HCl soln. see (3).]

[ $\bar{C}$  on reduction might be expected to give 2-chloro-1,4-dihydroxynaphthalene [Beil. VI-975], m.p. 116-117°; note, however, that this reaction has not actually been reported and that this prod. is also obtained by SO<sub>2</sub> reduction of 3-chloronaphthoquinone-1,2 (3:4704). — For study of oxidn.-reductn. potential of  $\bar{C}$  see (7).]

[ $\bar{C}$  with Cl<sub>2</sub> in AcOH gives (4) (5) 2,3-dichloronaphthoquinone-1,4 (3:4857).]

[ $\bar{C}$  in boilg. alc. with aq. NaN<sub>3</sub> splits out NaCl giving (90% yield (11)) 2-azidonaphthoquinone-1,4, long yel. pr. from alc., m.p. 118° dec.]

$\bar{C}$  with aniline on htg. (5) (6) in alc. soln. (8) (9) gives 3-chloro-2-anilino-naphthoquinone-1,4 [Beil. XIV-168, XIV<sub>1</sub>-(434)], red ndls., m.p. 207-208° (10), 207° (8), 202-203° (9) (6).

$\bar{C}$  like many other quinones is able to form Diels-Alder type adducts with many conjugated dienes [e.g.,  $\bar{C}$  with 2,3-dimethylbutadiene-1,3 (1:8050) gives an adduct which with aq. 5% NaOH and a little Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> at 70° reduces (with loss of halogen) to 2,3-dimethyl-1,4-dihydronaphthoquinone which in turn upon oxidn. with air at 0° gives (12) 2,3-dimethylanthraquinone [Beil. VII-815, VII<sub>1</sub>-(425)], yel. ndls. from alc. or AcOH, m.p. 210° (13), 209° (14), 208-209° (15), 208° (16), 205-206° (17); note also that this 2,3-dimethylanthraquinone is also obtd. (18) from the initial adduct with pyridine in absence of nir, or (18) from  $\bar{C}$  + 2,3-dimethylbutadiene-1,3 (1:8050) at 100-105° under press. — For behavior of  $\bar{C}$  with 2-methylbutadiene-1,3 (isoprene) (1:8020) and with butadiene-1,3 see (18).]

— 2-Chloronaphthoquinone-1,4-oxime-4 (2-chloro-4-nitrosonaphthol-1) [Beil. VII-729]; ndls. from alc., m.p. 200° dec. (8). [From  $\bar{C}$  with NH<sub>2</sub>OH.HCl in alc. on warming (8).]

— 2-Chloronaphthoquinone-1,4-(*p*-nitrophenylhydrazine-4) = 4-(*p*-nitrobenzeneazo)-2-chloronaphthol-1: m.p. 274° dec. (1). [From  $\bar{C}$  with *p*-nitrophenylhydrazine (1); also from 2-chloronaphthol-1 (3:1490) in alk. soln. on coupling with diazotized *p*-nitroaniline (1).]

3:3580

J. Chem

Zincke,

Russig, J. prakt. Chem. (2) 62, 41-42 (1900).

1875 (1924). (8) Cleve, Ber. 23, 955 (1890).

mann. Ber. 15, 485, Note 1 (1882).

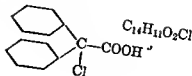
{2} Hodgson, Elliott.

41, 201, 338 (1927). (4)

1036-1039 (1888). (6)

3:3585  $\alpha$ -CHLORO-DIPHENYL-  
ACETIC ACID  
(Diphenylchloroacetic acid)

## SOLIDS



3:3585

Beil. IX - 674  
IX<sub>1</sub>-(282)

M.P. 120° dec. (1)  
118-119° dec. (2) (3)

[See also  $\alpha$ -chlorodiphenylacetyl chloride (3:0885).]

TbIs. from  $C_6H_5$ /Igr.; very eas sol. Igr.  
[For prepn. of  $\bar{C}$  from benzoic acid ( $\alpha$ -hydroxydiphenylacetic acid) (1:0770) with  $POCl_3$

on warming (not boil) until red color begins to appear (65% yield (3)) (4); with  $PCl_5$  (62.5% yield (1)) or with  $SOCl_2$  (3 moles) both at room temp; with  $SOCl_2$  directly at room temp. (92% yield (1)) or with  $SOCl_2$  (3 moles) in  $CCl_4$  at ord. temp (5) (2) see indic. refs; note, however, that benzoic acid (1:0770) with  $PCl_5$  at room temp. (1) gives instead  $\alpha$ -chlorodiphenylacetyl chloride (3:0885), m.p. 50°; note also that benzoic acid (1:0770) with large excess (6 moles)  $SOCl_2$  refluxed for several days gives (5)  $\alpha$ -chlorodiphenylacetic acid anhydride (Beil. IX<sub>1</sub>-(228)), m.p. 129° (5)]

[For prepn. of  $\bar{C}$  from *O*-carbomethoxybenzoic acid (2) with  $SOCl_2$  see (2); for prepn. of  $\bar{C}$  from  $\alpha$ -chlorodiphenylacetyl chloride (3:0885) by hydrolysis (even in moist air) see (8)]

$\bar{C}$  on reduction with  $TiCl_3$  in boil. AcOH gives (8) diphenylacetic acid (1:0765), m.p. 148°.

$\bar{C}$  (or its sodium salt) htd. under reduced press. at 125° for 10 hrs. gives (80-90% yield (9)) benzilide (Beil. XIX-187, XIX<sub>1</sub>-(700)), ndIs. from alc., m.p. 196° (10), 194° (11) (5), 103° (12), 192-193.5° (9) [the structure of this prod is disputed, but it is either 2,2,5,5-tetraphenyl-3,6-diketodioxane-1,4 or tetraphenyldiglycolic acid anhydride].

$\bar{C}$  with nq. KSH (or NaSH) does not (21) give the expected  $\alpha$ -mercaptodiphenylacetic acid (diphenylthioglycolic acid) (thiobenzoic acid) [Beil. XI<sub>1</sub>-(154)], but rather (apparently because of alkalmty of the soln) gives (13)  $\alpha$ -methoxydiphenylacetic acid (benzoic acid *O*-methyl ether) [Beil. XI<sub>1</sub>-(152)], m.p. 100° (13); note that various compounds prepd by a wide

variety of methods but all supposed to have this structure have been reported with m.p.'s as follows: 99-100° (14), 102° (15), 106° (16), 107° (17), 111-112° (18), 120-121° (9); note also that the corresp. methyl ester, viz., methyl  $\alpha$ -methoxydiphenylacetate, oil, b.p. 199-200° at 27 mm., has been prepd. (19) from  $\alpha$ -bromodiphenylacetate, oil, b.p. 199-200° from ether, m.p. 114-115° (20) (8), (13)  $\alpha$ -ethoxydiphenylacetic acid [Beil. XI<sub>1</sub>-(152)], viz., ethyl  $\alpha$ -ethoxydiphenylacetate, appears to be unreported]

$\bar{C}$  with  $Nn$  phenolate might be expected to give  $\alpha$ -phenoxydiphenylacetic acid, but neither this reaction nor the expected prod. is reported. — However,  $\bar{C}$  with thiophenol in  $C_6H_6$  refluxed 2 hrs evolves  $HCl$  and gives (22)  $\alpha$ -thiophenoxydiphenylacetic acid, but from 50%  $AcOH$ , m.p. 126-128° (22)

[ $\bar{C}$  with  $C_6H_5$  +  $AlCl_3$  gives normal Friedel-Crafts type reaction giving (25% yield (3)) triphenylacetic acid [Beil. IX-712, IX<sub>1</sub>-(309)], m.p. 265°.]

$\bar{C}$  with various amines or amino compds splits out  $HCl$  giving the corresp.  $\alpha$ -aminodiphenylacetic acid derivatives (e.g.,  $\bar{C}$  with  $NH_3$  gives (13)  $\alpha$ -aminodiphenylacetic acid, m.p. 180° (13); for other cases see (13)).

$\bar{C}$  with benzhydrazide in  $C_6H_6$  splits out  $HCl$  and yields (8)  $\alpha$ -benzhydrazido-diphenylacetic acid, m.p. 167-168° (8).

$\bar{C}$  with excess  $SOCl_2$  on warming does *not* give the expected  $\alpha$ -chlorodiphenylacetyl chloride (3:0885), m.p. 50°, but rather (5)  $\alpha$ -chlorodiphenylacetic acid anhydride, m.p. 120° (5).

$\bar{C}$  in pyridine on htg. at 100° (23) evolves  $CO_2$  presumably yielding benzoydryl chloride ( $\alpha$ -chlorodiphenylmethane) (3:0060) as its quaternary salt with pyridine.

— Methyl  $\alpha$ -chlorodiphenylacetate: oil, b.p. 196° at 16 mm. (4). [From  $\bar{C}$  in dioxane soln. with dimethoxyethane (100% yield) (4); note also that this ester with  $Cu$  bronze refluxed in  $C_6H_6$  for 5 hrs. then evaporated in air gives (4) the peroxide, m.p. 151-152°, of dimethyl tetraphenylsuccinate.]

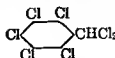
— Ethyl  $\alpha$ -chlorodiphenylacetate: cryst. from nlc., m.p. 43-44° (24) (6), b.p. 185° at 14 mm. (24). [From  $\bar{C}$  with  $EtOH + dry HCl$  (10) best in pres. of  $C_6H_6$  as directed (90% yield (25)), or from  $\alpha$ -chlorodiphenylacetyl chloride (3:0885) with  $EtOH$  (6), or from ethyl benzilate (1:2086) with  $PCl_5$  (6).]

—  $\alpha$ -Chlorodiphenylacetamide: m.p. 115° (6), 111-113° (26). [From  $\alpha$ -chlorodiphenylacetyl chloride (3:0885) in ether with  $NH_3$  gas (6) (13).]

—  $\alpha$ -Chlorodiphenylacetanilide: m.p. 88°. [See text of  $\alpha$ -chlorodiphenylacetyl chloride (3:0885).]

3:3585 (1) Setlur, Nadkarny, *Proc. Indian Acad. Sci.* 12-A, 268 (1940); *C.A.* 35, 1398 (1941).  
(12) Staudinger, *Ber.* 44, 545-547 (1911). (13)  
12-A, Pt. 3, 68-70 (1943); *C.A.* 38, 3250, 1739  
(14) Staudinger, *Ber.* 44, 547-548 (1911).  
1, 465-466 (1929). (22) Bistrzycki, *Riel. Helv.*  
*Veneto sci.*, Ser. II, 94, 167-182 (1935); *Cent.*  
1937, II 3605; not in *C.A.* (24) Klunger, *Ann.* 339, 262-263 (1912). (25) Adickes, *J. prakt.*  
*Chem.* (2) 150, 91 (1938). (26) Steinkopf, *Ber.* 41, 3593 (1908).

### 3:3590 PENTACHLOROBENZAL (DI)CHLORIDE



$C_7HCl_7$  Beil. V - 304  
V<sub>1</sub>-(153)  
V<sub>2</sub>—

M.P. 119.5° (1) B.P. 334° (2)  
109° (2) 109° cor. at 13 mm. (3)

Colorless lfts. from nlc.; eas. sol. hot, spar. sol. cold, alc.

[For prepn. of  $\bar{C}$ : (3:6327) with  $Cl_2$  at 210-230° as directed (70-80% yield) (1) (di)chloride (3:6327) with  $Cl_2$  in pres. of  $I_2 +$  (1) [Beil. VII-576, VII-323]] with  $PCl_5$  (2 moles) at 230° for 12-16 hrs. (together with hexachlorobenzene (3:4939)) see (1).]

$\bar{C}$  is unaffected by nq. even in s.t. at 300°; however,  $\bar{C}$  on hydrolysis with conc.  $H_2SO_4$

at 60-100° or with fumg.  $\text{H}_2\text{SO}_4$  at 40-50° gives (90% yield (3)) (4) pentachlorobenzaldehyde (3:4892), m.p. 202.5° (3).

3:3590 (1) Zincke, von der Linde, *Ber.* 26, 318 (1893). (2) Beilstein, Kuhlberg, *Ann.* 150, 306-308 (1869). (3) Lock, *Ber.* 66, 1533 (1933). (4) Bayer and Co., *Ger.* 243, 416, Feb. 10, 1912; *Cent.* 1912, I 618, [*C.A.* 6, 2292 (1912)]; U.S. 998,140, July 18, 1911; [*C.A.* 5, 2904-2905 (1911)].

### 3:3600 1,6-DICHLORONAPHTHOL-2



$\text{C}_{10}\text{H}_6\text{OCl}_2$  Beil. VI —  
VI<sub>1</sub>—  
VI<sub>2</sub>-(604)

M.P. 119.5° (1)

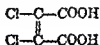
Ndls from hot lgr.

[For prepn from 1-chloronaphthol-2 (3:1700) by actn. of  $\text{Cl}_2$  in sunlight see (1).]

$\bar{\text{C}}$  on reduction with  $\text{FeSO}_4 + \text{NaOH}$  yields (2) 6-chloronaphthol-2 (3:3500), m.p. 115° (2).

3:3600 (1) Ruggli, Knapp, Merz, Zimmermann, *Helv. Chim. Acta* 12, 1050-1051 (1929). (2) Herzberg, Spengler, Schmidt (to I G.), *Ger.* 431,165, June 30, 1926, *Cent.* 1926, II 1106.

### 3:3634 DICHLOROMALEIC ACID



$\text{C}_2\text{H}_2\text{O}_4\text{Cl}_2$  Beil. II - 753  
II<sub>1</sub>—  
II<sub>2</sub>—

M.P. 119-120° (1)

118.5-119° (2)

118-119° (3)

116° (4)

[See also dichloromaleic anhydride (3:3635) and dichloromaleyl (di)chloride (3:6197).]

Ndls. from lgr./ether. — Eas. sol. aq.; sol. alc., AcOH; insol.  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ ,  $\text{CS}_2$ . — Note that  $\bar{\text{C}}$  on hgt. very readily loses  $\text{H}_2\text{O}$  and is converted to dichloromaleic anhydride (3:3635); the m.p.'s observed for  $\bar{\text{C}}$  are probably actually those of its anhydride.

Note also that, although the structure corresp. to  $\bar{\text{C}}$  should be capable of existing also in the geometrically isomeric *trans* configuration, no such dichlorofumaric acid or its derivatives has ever been reported.

[For prepn. of  $\bar{\text{C}}$  from furfural (1:0185) in conc.  $\text{HCl}$  soln. with  $\text{Cl}_2$  (30% yield) see (5); from dichloromaleinaldehyde-acid ("mucochloric acid") [Beil. III-727] by oxidn. with fumg.  $\text{HNO}_3$  on stdg. at ord. temp. for several days (100% yield (4)) (2) see indic. refs.; from  $\alpha,\beta$ -dichloro- $\beta$ -(trichloroacetyl)acrylic acid ("perchloro- $\beta$ -acetylacrylic acid") [Beil. III-733] by hydrolytic cleavage with aq.  $\text{NaOH}$  (chloroform is also formed) see (3); from hexachlorocyclohexen-1-dione-3,6 [Beil. VII-574] by hydrolytic cleavage with 10% aq.  $\text{NaOH}$  (trichloroethylene (3:5170) is also formed) see (1); from hexachlorocyclohexen-1-dione-3,5 ("hexachlororesorcinol") (3:3470) (6) or from 2,2,3,4,6,6-heptachlorohexen-3-one-5-acid-1 [Beil. III-735, III<sub>1</sub>-(255)] (6) with large excess dil. aq.  $\text{Ca}(\text{OCl})_2$  see indic. refs.]

[For formn. of  $\bar{\text{C}}$  from 3,4-dichlorofuroic acid [Beil. XVIII-282] by oxidn. with boilg. dil.  $\text{HNO}_3$  (7) or from 3,4,5-trichlorofuroic acid [Beil. XVIII-283] by oxidn. with hot dil.  $\text{HNO}_3$  or cold  $\text{Br}_2/\text{aq.}$  (7) see indic. refs.; from pyrrole with aq.  $\text{NaOCl}$  (other prods. are also formed) see (8).]

$\bar{C}$  behaves normally as a dibasic acid: e.g.,  $\bar{C}$  on titration with standard dil. aq. alk. gives Neut. Eq. 92.5 (2).

[Salts: for  $Li\bar{A}$ ,  $Na_2\bar{A} \cdot H_2O$ ,  $NaH\bar{A} \cdot H_2O$ ,  $K_2\bar{A} \cdot 2H_2O$ ,  $K\bar{A} \cdot H_2O$ ,  $Cu\bar{A} \cdot H_2O$ ,  $Pb\bar{A} \cdot H_2O$ ,  $Ni\bar{A} \cdot 2H_2O$  see (4). —  $Ba\bar{A} \cdot 2\frac{1}{2}H_2O$  (3). —  $Ag_2\bar{A}$ , white ndls. which explode on htg. (3) (8) (9).]

— Dimethyl dichloromaleate: oil, b.p. 225° (9). [From dichloromaleic anhydride (3:3635) in MeOH with HCl gas on boilg. (9). — This prod. with aniloe at 100° yields (4) dimethyl  $\alpha,\beta$ -dianilinomaleate, cryst. from alc., m.p. 172° (4).]

— Diethyl dichloromaleate: unreported.

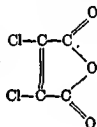
— Dichloromaleinimide [Beil. XXI-401]: ndls. from aq., m.p. 179° (10). [From dichloromaleic anhydride (3:3635) with urea on htg. at 110-115° (10).]

— *N*-Phenyldichloromaleinimide (dichloromalecanil) [Beil. XXI-402]: colorless lfts. from MeOH, m.p. 263°. [Reported only by indirect means.]

— Dichloromaleic dianilide: see under text of dichloromaleyl (di)chloride (3:6197).

3:3634 (1) Zincke, Fuchs, *Ann.* 267, 19-22 (1892). (2) Stelling, *Z. physik. Chem.* B-24, 424 (1934). (3) Zincke, von Lohr, *Ber.* 25, 2230 (1892). (4) Salmony, Simonis, *Ber.* 38, 2588-2590, 2594-2595, 2598-2599 (1905). (5) Leder, *Russ.* 48, 297, Aug. 31, 1930; *Cent.* 1937, II 288. (6) Zincke, Fuchs, *Ber.* 26, 509-510 (1893). (7) Hill, Jackson, *Am. Chem. J.* 12, 43-44, 124-125 (1890). (8) Ciamician, Silber, *Ber.* 17, 1743-1744 (1884). (9) Kauder, *J. prakt. Chem.* (2) 31, 5-6 (1885). (10) Dunlap, *Am. Chem. J.* 18, 333-334 (1890).

### 3:3635 DICHLOROMALEIC ANHYDRIDE



$C_4O_3Cl_2$  Bell. XVII-434  
XVII<sub>1</sub>—

M.P. 110-120° (1) (2)

110.5° (3)

110° (4) (8)

117-118° (5)

[See also dichloromaleic acid (3:3634).]

Colorless lfts. very eas. sol. alc., ether,  $C_6H_6$ , or  $CS_2$ ; sublimable.

[For prepn. of  $\bar{C}$  from dichloromaleic acid (3:3634) by litg. see (1) (2) (10); for prepn. of  $\bar{C}$  from maleic anhydride (1:6625) with  $Cl_2$  at 136° in pres. of Fe (80% yield (7)) or from chlorofumaryl dichloride with  $Cl_2$  in pres. of Fe (8) see indic. refs.; for prepn. of  $\bar{C}$  from furoic acid (1:0476) by conv. with  $MnO_2 + HCl$  to mucochloric acid,  $OCH.CCl=CCl.COOH$  [Beil. III-727] (9), and subsequent treatment with fumg.  $HNO_3$  (4) (9) or from 3,4-dichlorofuran (9) by oxidn. with fumg.  $HNO_3$  (9) see indic. refs.; for formo. of  $\bar{C}$  (together with other products) from diethyl tartrate (1:4256) with  $PCl_5$  for 7-8 hrs. at 100° see (6); from either dichloromaleo(di)nitrile (m.p. 58-59°,  $D_4^{62} = 1.32561$ ,  $n_D^{25} = 1.48824$  (12)) or from dichlorofumaro(di)nitrile (m.p. 66.0-60.5°,  $D_4^{62} = 1.32543$ ,  $n_D^{25} = 1.48845$  (12)) by hydrol. see (12).]

$\bar{C}$  is itself spar. sol. aq. but slowly dissolves (1) (6) yielding a soln. of dichloromaleic acid (3:3634).

$\bar{C}$  with  $PCl_5$  yields (8) dichloromaleyl dichlorido (3:6197).

$\bar{C}$  with 1 mole anthracene (1:7285) htd. for 10 min. at 176° gives 100% yield (4) of anthracene-9,10-endo-dichloromaleic anhydride, ndls. from acetonitrile, m.p. 235° (4).

$\bar{C}$  with 1 mole urea htd. to 90-95° for 20 min. yields (11) dichloromaleic acid monoureide [Beil. III-68], m.p. 158° dec. (11); this prod. on fusion or the original system htd. at 110-115° yields (11) dichloromaleimide [Beil. XXI-401], m.p. 179° (11).

$\bar{C}$  on hgt. with aniline (9) yields  $\alpha$ -chloro- $\alpha$ -aminomalein- $\alpha'$ -isoanil [Beil. XVII-555], greenish yel. cryst. from alc., m.p. 188.7-190.2° cor. (9), 187° (10).

3:3635 (1) Ciamician, Silber, *Ber.* 16, 2396 (1853). (2) Zincke, Fuchs, *Ann.* 267, 20-22 (1892). (3) Kauder, *J. prakt. Chem.* (2) 31, 4 (1855). (4) Diels, Thiele, *Ber.* 71, 1173-1178 (1938). (5) Leder, *J. prakt. Chem.* (2) 130, 271 (1931). (6) Patterson, Todd, *J. Chem. Soc.* 1939, 1768-1771. (7) Leder, *Russ. Acad. Sci.* 43, 419, June 30, 1935, *Cent.* 1936, I 1310, *C. A.* 31, 7447 (1937). (8) Vandeveldt, *Bull. acad. roy. Belg.* (3) 37, 660-700 (1900); *Cent.* 1900, I 404. (9) Shepard, Winslow, Johnson, *J. Am. Chem. Soc.* 52, 2088-2089 (1930). (10) Salmony, Simons, *Ber.* 38, 2538 (1905).

(11) Dunlap, *Am. Chem. J.* 18, 333-334 (1896). (12) Mommaerts, *Bull. classe sci., Acad. roy. Belg.* (5) 27, 579-597 (1944), *Cent.* 1943, I 615-616, *C. A.* 38, 3621 (1944).

### 3:3665 2,3-DICHLORONAPHTHALENE


 $C_{10}H_6Cl_2$ 

Beil. V - 544

 $V_1$ 
 $V_2$ -(446)

M.P. 120° (1)  
119.5-120.5° (2)  
119.5° (4)

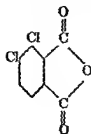
Spar. sol. cold, eas. sol. hot alc. or ether.

[For prepn. of  $\bar{C}$  from naphthalenetetrachloride-1,2,3,4 (3:4750) by hgt. with  $Ag_2O$  in s.t. at 200° (1) or (in small yield together with other prods.) by hgt. with alc. KOH (3) (4) see indic. refs.; from 1,2,3-trichloronaphthalene (3:2125) with Na/Hg in alc. see (4).]

[ $\bar{C}$  on monosulfonation in  $CS_2$  with  $ClSO_3H$  yields (4) mainly 2,3-dichloronaphthalene-sulfonic acid-8 [Beil. XI-164] (corresp. sulfonyl chloride, m.p. 142°, corresp. sulfonamide m.p. 268°) accompanied by 2,3-dichloronaphthalenesulfonic acid-6 (?) [Beil. XI-183] (corresp. sulfonyl chloride, m.p. 173°).]

3:3665 (1) Leeds, Everhart, *J. Am. Chem. Soc.* 2, 210-212 (1880). (2) Hampson, Weissberger, *J. Chem. Soc.* 1936, 394. (3) Widman, *Ber.* 15, 2162 (1882). (4) Armstrong, Wynne, *Chem. News* 61, 273-275, 284 (1890).

### 3:3695 3,4-DICHLOROPHTHALIC ANHYDRIDE


 $C_8H_2O_3Cl_2$ 

Beil. XVII - 483

 $XVII_1$ -(253)

M.P. 120-121° cor. (1)  
120-121° (2)

[See also 3,4-dichlorophthalic acid (3:4880).]

TbIs. from  $CCl_4$ ; sol. in  $C_6H_6$ , toluene,  $CHCl_3$ .

[For prepn. of  $\bar{C}$  from 3,4-dichlorophthalic acid (3:4880) by protracted hgt. at 220° see (2); for formn. of  $\bar{C}$  (together with other isomers) from phthalic anhydride (1:0725) with  $Cl_2$  at 240° in pres. of Fe or Fe salts (3), from phthalic anhydride or 3-chlorophthalic

anhydride (3:3900) with  $\text{Cl}_2$  in fuming  $\text{H}_2\text{SO}_4$  in pres. of  $\text{I}_2$  (4) (1), [see indic. refs.] [For sepn. of  $\bar{\text{C}}$  from isomeric dichlorophthalic anhydrides by means of salts of corresp. acids see (4) (1) (18); by means of differential hydrolysis with  $\text{H}_2\text{SO}_4$  (prods. with no  $\alpha$ -chlorine such as 4,5-dichlorophthalic anhydride require  $\text{H}_2\text{SO}_4$  of 98-100% concn.; those with one  $\alpha$ -chlorine such as  $\bar{\text{C}}$  hydrolyze with 56-95%  $\text{H}_2\text{SO}_4$ ; those with two  $\alpha$ -chlorines such as 3,6-dichloro- or 3,4,5,6-tetrachlorophthalic anhydrides hydrolyze at  $\text{H}_2\text{SO}_4$  concns. of less than 50%) see (5).]

$\bar{\text{C}}$  dislvd. in abs. alc. yields one of the two known acid esters, viz., 3,4-dichloro-2-carbethoxybenzoic acid, pr. from dil. alc., m.p.  $164^\circ$  (6); see also under 3,4-dichlorophthalic acid (3:4880).

[ $\bar{\text{C}}$  with  $\text{PCl}_5$  htd. in a.t. at  $200^\circ$  for 6 hrs. gives exclusively (6) *pseudo*-3,4-dichlorophthaloyl dichloride (3,3,6,7-tetrachlorophthalide), ndls. from  $\text{C}_6\text{H}_6$ , m.p.  $123^\circ$  (6) (this prod. shaken with abs. alc. susp. of  $\text{CaCO}_3$  for 10 hrs. yields (6) 6,7-dichloro-3,3-diethoxyphthalide, pr. from pet. ether., m.p.  $79^\circ$  (6), which depresses m.p. of normal diethyl 3,4-dichlorophthalate, m.p.  $80^\circ$  (6) to  $60^\circ$ ).]

$\bar{\text{C}}$  with 1 mole  $\text{NH}_2\text{OH}\cdot\text{HCl} + \text{Na}_2\text{CO}_3$  in aq. as directed (2) yields 3,4-dichlorophthalylhydroxylamine (*N*-hydroxy-3,4-dichlorophthalimide) [Beil. XXI-504], ndls. from  $\text{MeOH}$ , m.p.  $218-219^\circ$  (2),  $216-219^\circ$  (7) (this prod. with boilg. aq.  $\text{Na}_2\text{CO}_3$  yields (2) (7) a mixt. of 3,4-dichloro-2-aminobenzoic acid (3,4-dichloroanthranilic acid) [Beil. XIV-367, XIV-549] and 5,6-dichloro-2-aminobenzoic acid (5,6-dichloroanthranilic acid) [Beil. XIV-368]).]

[ $\bar{\text{C}}$  with steam passed over cat. at  $380-420^\circ$  loses  $\text{CO}_2$  presumably yielding (8) 2,2-dichlorobenzoic acid (3:4650) and/or 3,4-dichlorobenzoic acid (3:4925).]

[ $\bar{\text{C}}$  with hydroquinone (1:1500) +  $\text{H}_3\text{BO}_3$  htd. at  $100^\circ$  and afterward treated with hot conc.  $\text{H}_2\text{SO}_4$  (9), or  $\bar{\text{C}}$  with  $\text{AlCl}_3 + \text{NaCl}$  htd. at  $200-220^\circ$  for 45 min. (10), or  $\bar{\text{C}}$  with *p*-chlorophenol (3:0475) htd. with fuming  $\text{H}_2\text{SO}_4 + \text{H}_3\text{BO}_3$  (11), gives 5,6-dichloro-1,4-dihydroxyanthraquinone (5,6-dichloroquinizarin) [Beil. VIII-715], red. ndls. from  $\text{AcOH}$ , m.p.  $230^\circ$  (10),  $208^\circ$  (9) (diacetate, m.p.  $179^\circ$  (10),  $140^\circ$  (9)).]

[For study of behavior of  $\bar{\text{C}}$  with *o*-chlorotoluene +  $\text{AlCl}_3$  see (12); for use of  $\bar{\text{C}}$  with dibenzanthrone derivs. in prepn. of vat dyes see (13); for reactn. with *p*-cresol see (16).]

$\bar{\text{C}}$  on fusion with urea yields (14) 3,4-dichlorophthalimide, m.p.  $348-351^\circ$  (14) (for use in prepn. of pigments of phthalocyanine type see (14) (15)).]

$\bar{\text{C}}$  (1 pt.) dislvd. in 5 pts. boilg.  $\text{AcOH}$  and treated with 1 pt. aniline gives on cooling 97% yield 3,4-dichlorophthalanil [Beil. XXI-(391)], cryst. from  $\text{AcOH}$ , m.p.  $181-181.5^\circ$  cor. (1), ndls. from alc., m.p.  $179-180^\circ$  (17) [note, however, that on protracted htg. with excess aniline one of the two nuclear halogens also reacts, e.g.,  $\bar{\text{C}}$  (1 pt.) boiled with 3 pts. aniline for 10 hrs. gives 4-chloro-3-anilinophthalanil, cryst. from alc., m.p.  $159.5-160^\circ$  cor. (1); note also that under certain conditions both halogens can be removed, e.g., 3,4-dichlorophthalanil (above) on refluxing 6 hrs. with aniline + anhydrous  $\text{Na}_2\text{CO}_3 + \text{Cu}$  gives (10% yield (17)) 3-anilinophthalanil, or.-yel. pr., m.p.  $144.5-145^\circ$  (17).]

$\bar{\text{C}}$  on saponification with standard alk. (Sap. Eq. = 108.5), followed by acidification, yields 3,4-dichlorophthalic acid (3:4880) q.v.

I 2533; 1930, I 1303. (13) Imperial Chem. Ind., Ltd., Shaw, Thomson, Brit. 383,624, Dec. 15, 1931; *Cent.* 1933, I 1358. (14) Imperial Chem. Ind., Ltd., Thorpe, Linstead, Brit. 390,149, Apr. 27, 1933; French 737,392, Dec. 10, 1932, *Cent.* 1933, II 794. (15) Thorpe, Linstead, Thomas (to Scottish Dyes, Ltd.), Brit. 389,842, Apr. 20, 1933; *Cent.* 1933, II 2769. (16) Knescheck, Ullmann, *Ber.* 55, 306, 315 (1922). (17) Marriott, Robinson, *J. Chem. Soc.* 1939, 137. (18) Hodgson, *J. Soc. Dyers Colourists* 49, 215 (1933).

### 3:3720 4-CHLORONAPHTHOL-1


 $C_{10}H_7OCl$ 

Beil. VI - 611

 VI<sub>1</sub>-(308)

 VI<sub>2</sub>-(582)

M.P. 120-121°	(1)
120-120.5°	(2)
120°	(3)
116-117°	(4) (26)
116°	(5)

Ndls. from dil. alc. or from  $CHCl_3$ . — Very eas. sol. org. solv. — Sublimes in ndls. — Volatile with steam but less so than 2-chloronaphthol-1 (3:1490) (use in sepn. from latter (5)).

[For prepn. of  $\bar{C}$  from bis-(4-chloronaphthyl-1) carbonate (itself obtd. from bis-( $\alpha$ -naphthyl) carbonate in AcOH with  $Cl_2$  in pres. of  $SbCl_5$  (5)) by hydrolysis with alc. KOH see (5); from 4-chloronaphthyl-1 *p*-toluenesulfonate (itself obtd. from  $\alpha$ -naphthyl *p*-toluenesulfonate in  $CCl_4$  with  $Cl_2$  + cat. (7)) by hydrolysis see (7); from  $\alpha$ -naphthol (1:1500) with  $SO_2Cl_2$  in  $CHCl_3$  as directed (yields: 20-60% (1), 42% (5), 27-33% (8)) (26) (the isomeric 2-chloronaphthol-1 (3:1490) is also formed) see indic. refs.; from 1,4-dichloronaphthalene (3:1655) by htg. with MeOH/KOH in copper-lined autoclave 20 hrs. at 190-200° see (9); from 4-chloronaphthol-1-sulfonic acid-8 (10) (3) by hydrolysis (10) or reductive cleavage with Na/Hg (3) of the  $-SO_3H$  group see indic. refs.; from 4-chloro-1-hydroxynaphthoic acid-2 (Beil. XI-(146)) by htg. in naphthalene or nitrobenzene in pres. of aniline (yield 81-89%) see (2); from 4-chloronaphthyl-1 MgBr in ether by oxidn. with dry  $O_2$  see (4).]

$\bar{C}$  with  $Cl_2$  in AcOH yields (4) 2,4-dichloronaphthol-1 (3:3250), m.p. 106° (4);  $\bar{C}$  with 1 mole  $Br_2$  in AcOH gives alm. quant. yield (11) 2-bromo-4-chloronaphthol-1; ndls., m.p. 96° (11).

[ $\bar{C}$  with 0.5 mole  $SCl_2$  in  $CHCl_3$  gives (79% yield (12)) bis-(4-chloro-1-hydroxynaphthyl-2) sulfide, colorless ndls. from hot alc., m.p. 172° dec. (12); for reactn. of  $\bar{C}$  with 2-hydroxynaphthalene-1-sulfonyl bromide (13) (14), or with  $SCl_2$  +  $\beta$ -naphthol (15), see indic. refs.]

[ $\bar{C}$  undergoes many condensations with various types of cpds., e.g., for condensation of  $\bar{C}$  with formaldehyde (16) (17), with 2,6-bis-(hydroxymethyl)-4-methylphenol (18), and use of prods. as mothproofing cpds. see indic. refs.; for condensation of  $\bar{C}$  with naphthalene-2,3-dicarboxylic acid anhydride [Beil. XVII-(266)] see (19); for condensation of  $\bar{C}$  with maleic acid (1:0450) or with ethyl acetoacetate (1:1710) or with ethyl methylacetoacetate (1:1712) using  $H_2SO_4$  or  $P_2O_5$  yielding naphthapyrone derivs. see (8); for condens. of  $\bar{C}$  with 2,3-dichloronaphthoquinone-1,4 (3:4357) for use in prepn. of vat dyes see (21).]

[ $\bar{C}$  with maleic anhydride (1:0625) +  $AlCl_3$  + NaCl htd.  $\frac{1}{2}$  hr. at 210-220° gives (13% yield (20)) 10-chloro-1-hydroxyanthraquinone-4,9, dark red ndls. from  $C_6H_6$ , m.p. 205-206°; similarly  $\bar{C}$  with citraconic anhydride (1:1135) yields (20) both 10-chloro-1-hydroxy-2-methyl- and 10-chloro-1-hydroxy-3-methylanthraquinone-4,9.]



[ $\bar{C}$  with 2,4-dinitrotoluene forms a mol. cpd., m.p.  $65^{\circ}$  (22);  $\bar{C}$  with 2,4-dinitroanisole forms a mol. cpd. (22); for use of these as fungicides see (22); for use of  $\bar{C}$  as disinfectant see (23).]

$\bar{C}$  with  $\text{KOH}$  in  $\text{CHCl}_3$  (5) forms an unstable mol. cpd.,  $\bar{C}.\text{KOH}$ , or. ndls., m.p.  $171^{\circ}$  (5),  $170-171^{\circ}$  (4) (1).

$\bar{C}$  with  $\text{FeCl}_3$  or  $\text{Cu}(\text{OCl})_2$  in neutral soln. gives blue ppt. (5) (4).

$\bar{C}$  in alc. (10 pts.) treated with conc.  $\text{HCl}$  (5 pts.) and then with  $\text{NaNO}_2$  (0.4 pt.) yields (2) 4-chloronaphthoquinone-1,2-oxime-2 [Beil. VII<sub>1</sub>- (385)], purified via the beautifully crystg. dif. sol. red sodium salt, from which  $\text{HCl}$  ppts. the free oxime, pale yel. ndls., m.p.  $157^{\circ}$  (2).

① 4-Chloro-1-naphthyl acetate: cryst. from lgr., m.p.  $44^{\circ}$  (4) (26). [From  $\bar{C}$  with  $\text{AcCl}$  (2).] [For Fries rearr. of this acetate to 4-chloro-1-hydroxy-2-naphthyl methyl ketone see (24).]

— 4-Chloro-1-naphthyl benzoate: ndls. from nlc., m.p.  $100-101^{\circ}$  (25). [Reported only by indirect means (25).]

3:3720 (1) Kast, *Ber.* 44, 1337 (1911). (2) Reissert, *Ber.* 44, 867-869 (1911). (3) Friedländer, Karamessinis, Schenk, *Ber.* 55, 50 (1922). (4) Bodroux, *Bull. soc. chim.* (3) 31, 35-36 (1904). (5) 3053 (1895). (6) Lesser, *Gad. Ber.* 56, 972-973 (1923). Ger. 240,038, Oct. 26, 1911; *Cent.* 1911, II 1565. (8) Soc. 13, 651-653 (1930). (9) Soc. d'exploitation des brevets O. Matter, French 807,536, Jan. 14, 1937; *Cent.* 1937, I 4560; *C.A.* 31, 5382 (1937). (10) Kalle and Co., Ger. 313,147, Oct. 23, 1921; *Cent.* 1922, II 144.

3:3750 2,6-DICHLOROBENZO-  
QUINONE-1,4  
(*m*-Dichlorobenzoquinone)



$\text{C}_6\text{H}_2\text{O}_2\text{Cl}_2$

Beil. VII - 633  
VII<sub>1</sub>-(347)

M.P.  $121^{\circ}$  cor. (1)  
 $121^{\circ}$  (2)  
 $120.5^{\circ}$  (3)  
 $120^{\circ}$  (4) (5) (6)  
 (9) (14) (17)  
 $120-121^{\circ}$  (7) (8)  
 $119^{\circ}$  (12)

[See also 2,6-dichlorohydroquinone (3:4600).]

Yellow cryst. from  $\text{C}_6\text{H}_6$  or lgr.; yellow pr. from nlc. or  $\text{AcOH}$ . —  $\bar{C}$  is somewhat sol. boulg. aq. or cold alc.; cas. sol. hot alc.; sol.  $\text{CHCl}_3$ . — Sublimes far below m.p.; volatile

with steam. —  $\bar{C}$  turns skin reddish brown. [For study of photochem. decompn. of alc. soln. see (43)]

[For prepn. of  $\bar{C}$  from 2,6-dichlorohydroquinone (3:4600) with  $\text{CrO}_3$  (7) or with excess aq.  $\text{FeCl}_3$  soln. on warming (9) see indic. refs.; from 2,4,6-trichlorophenol (3:1673) on oxidn. with  $\text{CrO}_3$  in  $\text{AcOH}$  at 30–40° (yields: 69% (3), 27% (10)) (2), with cold fumg.  $\text{HNO}_3$  (25% yield (11)) (6), with mixt. of fumg.  $\text{HNO}_3$  + conc.  $\text{H}_2\text{SO}_4$  (12), with  $\text{PbO}_2$  in  $\text{AcOH}$  or in  $\text{C}_6\text{H}_6$  (10) or in alc. with  $\text{HNO}_2$  (13) (14) cf. (10), see indic. refs. (note that in addn. to  $\bar{C}$  the crude oxidn. prod. contains also 2-chloro-6-(2',4',6'-trichlorophenoxy)-benzoquinone-1,4, m.p. 134–135° (10), and 2,6-bis-(2',4',6'-trichlorophenoxy)benzoquinone-1,4, m.p. 245° (10), which resemble  $\bar{C}$  in appearance, composition, and behavior); from 2,6-dichloro-4-fluorophenol (8) or its dimethyl ether (8) or from 2,6-dichloro-4-bromophenol (11) with ice-cold  $\text{HNO}_2$  ( $D = 1.5$ ) see indic. refs.; from 2,6-dichloro-4-nitrophenol [Beil. VI-241, VI-122)] on htg. above its m.p. (125°) (15) or in small amt. with mixt. of fumg.  $\text{HNO}_3$  + fumg.  $\text{H}_2\text{SO}_4$  at ord. temp. (16); from 2,6-dichloro-4-aminophenol [Beil. XIII-512, XIII-183)] by oxidn. with  $\text{K}_2\text{Cr}_2\text{O}_7$  +  $\text{H}_2\text{SO}_4$  (90% yield (1)) (17) see indic. refs.; from 3,5-dichloro-4-aminophenol [Beil. XIII-513] similarly see (18); from 2,6-dichloro-*p*-phenylenediamine [Beil. XIII-118, XIII-37)] by oxidn. with dichromate see (19) (10); from 2,6-dichloro-4-bromophenol bromide (4) or from "2,4,6-trichlorophenol bromide" (2,4,6-trichloro-6-bromocyclohexadiene-1,4-one-3) [Beil. VII-145] (5) with cold fumg.  $\text{HNO}_3$  see indic. refs.; from 2,6-dichlorobenzoquinone-1,4-(2,4-dinitroanil)-4 [Beil. XII-754] on hydrolysis with dil.  $\text{H}_2\text{SO}_4$  in a.t. at 200° see (20).]

[For study of bactericidal value of  $\bar{C}$  see (21); for use as vulcanization accelerator see (22); for condensation with  $\beta$ -naphthylamine and use of prods. as intermediates in prepn. of sulfur dyes see (23); for condensation with various amines to yield corresp. mono- and diarylaminoquinones see (24); for condensation with various aminophenols and use of prods. in prepn. of oxazine dyes see (25); for condensation of  $\bar{C}$  with  $\alpha$ -aminoaryl mercaptans and use in prepn. of vat dyes see (26); for reactn. with  $\text{Na}_2\text{S}_2\text{O}_3$  +  $\text{AcOH}$  in prepn. of sulfur dyes see (40)]

$\bar{C}$  on reductn. with aq.  $\text{SO}_2$  gives (80% yield (3)) (27) (1) 2,6-dichlorohydroquinone (3:4600) (note, however, that  $\bar{C}$  in dil. aq.  $\text{NaOH}$  under  $\text{N}_2$  with  $\text{SO}_2$  is in part reduced to 2,6-dichlorohydroquinone (3:4600) and in part sulfonated to mono- and disulfonic acids of  $\bar{C}$  (28)). — [For studies of the oxidn.-reductn. potential of system  $\bar{C}$  + 2,6-dichlorohydroquinone see (3) (29) (30) (42).] — [ $\bar{C}$  forms with 2,6-dichlorohydroquinone the corresp. quinoxaline, brown prismatic ncls, m.p. 135° (31), but does so less readily than the benzoquinone-1,4/hydroquinone system (3); note that this same quinoxaline is obtd. (36) from  $\bar{C}$  + ord. hydroquinone (36).]

[ $\bar{C}$  in  $\text{CHCl}_3$  at low temp. does not react with  $\text{Cl}_2$  but at ord. temps. gives (22) tetrachlorobenzoquinone-1,4 (chloranil) (3:4978). —  $\bar{C}$  in  $\text{AcOH}$  at 15–20° gives (11) with 2 moles  $\text{Br}_2$  2,6-dichloro-3,5-dibromobenzoquinone-1,4 [Beil. VII-612], m.p. 291° (11), accompanied by a little 2,5-dichloro-3,6-dibromobenzoquinone-1,4 [Beil. VII-612], m.p. 292° (11); but  $\bar{C}$  in boilg.  $\text{AcOH}$  with 2 moles  $\text{Br}_2$  gives exclusively the latter (11) cf. (19) (33).]

[ $\bar{C}$  with conc.  $\text{HCl}$  gives on boilg. (34) both 2,3,5-trichlorobenzoquinone-1,4 (3:4672) and 2,3,5,6-tetrachlorobenzoquinone-1,4 (chloranil) (3:4978).]

[ $\bar{C}$  in cold alc. treated dropwise with 10% alc.  $\text{KOH}$  gives first a green soln. turning to brownish red and pptg. in poor yield (2) a potassium salt of 2-chloro-3,6-dihydroxybenzoquinone-1,4 [Beil. VIII-378];  $\bar{C}$  in satd. alc. soln. at 50–60° with conc.  $\text{NH}_4\text{OH}$  gives a purple soln. grad. turning brownish red and pptg. (20–25% yield (2)) 2-chloro-3,6-dihydroxybenzoquinone-1,4-diamide [Beil. VIII-370], bronze-colored lfts. from  $\text{AcOH}$ , subliming at 258–260° without melting]

[ $\bar{C}$  (1 pt.) in alc. (15–20 pts.) + conc.  $\text{HCl}$  (0.3–0.4 pts.) treated with aniline (0.25 pt.)

yields mainly (35) 2,6-dichloro-3-anilino-1,4-benzoquinone (3:4600) accompanied by small amts. of 2-chloro-3,6-dianilino-1,4-benzoquinone (see below);  $\bar{C}$  in either alc. or AcOH with excess aniline yields (35) 2-chloro-3,6-dianilino-1,4-benzoquinone (3:4600).] — [Note that  $\bar{C}$  with sulfanilic acid behaves similarly: e.g.,  $\bar{C}$  with 2 moles sulfanilic acid in aq. (best in pres. of NaOAc) yields (37) 2-chloro-3,6-bis-(p-sulfanilino)-1,4-benzoquinone (3:4600); in aq. alc., however, 2,6-dichloro-3-(p-sulfanilino)-1,4-benzoquinone is also formed (37).]

[ $\bar{C}$  with  $NH_2OH.HCl$  in alc. yields (38) 2,6-dichlorobenzoquinone-1,4-monoxime-4, pale yel. lfts. from dil. alc., m.p.  $140^\circ$  (38), which with cold conc.  $HNO_3$  oxidizes to 2,6-dichloro-4-nitrophenol [Beil. VI-241], colorless ndls. from aq., lfts. from AcOH, thls. from ether, m.p.  $125^\circ$  dec.; note that no dioxime can be formed.]

[ $\bar{C}$  with semicarbazide  $HCl$  in cold dil. alc. gives (39) 2,6-dichlorobenzoquinone-1,4-semicarbazone-4, in red or yel. forms acc. to conditions, but both of m.p.  $219^\circ$  dec. (39); note that no bis-semicarbazone can be formed.]

[ $\bar{C}$  with 20% soln. of triphenylphosphine in  $CHCl_3$  gives an orange-red, red, or brown color (41) (also shown by trichlorobenzoquinone and by chloranil); for other limitations and details see (41).]

3:3750 (1) van Erp, *Ber.* 58, 664-665 (1925). (2) Kehrman, Tiesler, *J. prakt. Chem.* (2) 40, 480-486 (1889). (3) Conant, Fieser, *J. Am. Chem. Soc.* 45, 2202-2204 (1923). (4) Kohn, Sussmann, *Monatsh.* 46, 586 (1925). (5) Kohn, Rabinowitsch, *Monatsh.* 48, 353 (1927). (6) Faust, *Ann.* 149, 153-155 (1869). (7) Den Hollander, *Rec. trav. chim.* 39, 481-482 (1920). (8) Hodgson, Nixon, *J. Chem. Soc.* 1930, 1868-1869. (9) Dakin, *Am. Chem. J.* 42, 491 (1909). (10) Hunter, Morse, *J. Am. Chem. Soc.* 48, 1615-1624 (1926).

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(21) Morgan, Cooper, *J. Soc. Chem. Ind.* 43-T, 352-354 (1924). (22) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; *Cent.* 1933, I 3133. (23) Thiess, Maennchen (to I.G.), *Ger.* 507,833, Sept. 20, 1930; *Cent.* 1930, II 2839. (24) Becke, W. Suida, *H. Suida, Ger. Pat.* 7, 920 (1874). (25) Becke, W. Suida, *H. Suida, Ger. Pat.* 7, 920 (1874).

(1934).

(31) Ling, Baker, *J. Chem. Soc.* 63, 1321-1322 (1893). (32) Oliveri-Tortorici, *Gazz. chim. ital.* 27, II 585-586 (1897). (33) Hantzsch, Schniter, *Ber.* 20, 2279-2282 (1887). (34) Levy, Schultz, *Ann.* 210, 153 (1881). (35) Niemeyer, *Ann.* 228, 334-337 (1885). (36) Siegmund, *J. prakt. Chem.* (2) 92, 361-362 (1915). (37) H. Suida, W. Suida, *Ann.* 416, 136-142 (1918). (38) H. Suida, W. Suida, *Ann.* 416, 136-142 (1918). (39) H. Suida, W. Suida, *Ann.* 416, 136-142 (1918).

Soc. 49,

293-297 (1927).

3:3780 4-CHLORO-3-HYDROXYBENZ-  
ALDEHYDE



$C_7H_5O_2Cl$  Beil. S.N. 746

M.P.  $121^\circ$  (1) (2)

Colorless ndls. (1).

[For prepn. of  $\bar{C}$  from *m*-hydroxybenzaldehyde (1:0055) via 4-nitro-3-hydroxybenzaldehyde, reduction to amino cpd., and use of appropriate diazo reactn. see (1).]

$\bar{C}$  in 50% AcOH mononitrated as specified (2) gives mainly 4-chloro-2-nitro-3-hydroxybenzaldehyde, spar. sol. in hot  $\text{CHCl}_3$ , colorless pr. from AcOH, m.p.  $175^\circ$  (2) (3). [Note that this statement takes account of a very important correction (3).] [This 4-chloro-2-nitro-3-hydroxybenzaldehyde yields the following derivs.: *p*-nitrophenylhydrazone, deep maroon ndls. from hot AcOH, m.p.  $275\text{--}276^\circ$  dec.; semicarbazone, lt. or. ndls. from alc., m.p.  $265\text{--}266^\circ$  dec. (2) ]

$\bar{C}$  in aq. contg.  $\text{NaHCO}_3$  treated with  $(\text{CH}_3)_2\text{SO}_4$  yields (1) 4-chloro-3-methoxybenzaldehyde, m.p.  $52^\circ$  (1). [This prod. depresses m.p. of corresp. methyl ether of the isomeric 2-chloro-3-hydroxybenzaldehyde (3:4085), m.p.  $56\text{--}57^\circ$  (1); on keeping it acquires a beautiful silver-gray color (1); it yields an oxime, colorless ndls., m.p.  $98\text{--}99^\circ$ , and a *p*-nitrophenylhydrazone, old-gold ndls., m.p.  $251^\circ$  (1).]

④ 4-Chloro-3-hydroxybenzaldehyde: colorless ndls. of hydrate, dec.  $106\text{--}110^\circ$  from dil. alc.; anhydrous oxime, m.p.  $126^\circ$  (1).

— 4-Chloro-3-hydroxybenzaldehyde phenylhydrazone: unrecorded.

④ 4-Chloro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazone: violet-red ndls. from dil. alc., m.p.  $226\text{--}227^\circ$  (1).

— 4-Chloro-3-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.

④ 4-Chloro-3-hydroxybenzaldehyde semicarbazone: pale yel. ndls., m.p.  $238\text{--}239^\circ$  (1).

3:3780 (1) Hodgson, Beard, *J. Chem. Soc.* 1926, 150-154. (2) Hodgson, Beard, *J. Chem. Soc.* 1926, 2033-2034. (3) Hodgson, Beard, *J. Chem. Soc.* 1927, 2377-2378.

### 3:3810 7-CHLORONAPHTHOL-1


 $\text{C}_{10}\text{H}_7\text{OCl}$ 

Beil. VI - 612

 $\text{VI}_1\text{—}$ 
 $\text{VI}_2\text{—}$ 

M.P.  $123^\circ$  (1)

Ndls. from aq. or  $\text{CS}_2$ ; spar. sol. aq. —  $\bar{C}$  has odor suggesting that of iodoform.

[For prepn. of  $\bar{C}$  from  $\gamma$ -(*p*-chlorophenyl)paraconic acid [Beil. XVIII-421] by distn. see (1) ]

$\bar{C}$  dis. in aq. alk. from which it is reprecipitated by  $\text{CO}_2$ ; the alk. soln. of  $\bar{C}$  couples with diazonium salts yielding azo dyestuffs (1).

$\bar{C}$  with aq.  $\text{FeCl}_3$  gives a yellowish white ppt. which on stdg. assumes a pronounced violet color (1)

$\bar{C}$  (1 mole) with  $\text{P}(\text{KOH})$  (1 mole) in  $\text{CHCl}_3$  yields an addn. cpd.,  $\bar{C} \cdot \text{P}(\text{KOH})$ , or.-red. ndls. from hot  $\text{CHCl}_3$ , m.p.  $139^\circ$  (1).

— 7-Chloro-1-naphthyl acetate: oil.

3:3810 (1) Erdmann, Kirchhoff, *Ann.* 247, 374-375 (1885).

### 3:3840 1,4-DICHLORONAPHTHOL-2


 $\text{C}_{10}\text{H}_6\text{OCl}_2$ 

Beil. VI - 650

 $\text{VI}_1\text{—}$ 
 $\text{VI}_2\text{—}$ 

M.P.  $123\text{--}124^\circ$  (1)

$122\text{--}123^\circ$  (2)

$121^\circ$  (3)

Ndls. from lgr; eas. sol. alc., ether, or AcOH.

[For prepn. of  $\bar{C}$  from 1,1-dichloro-2-keto-1,2-dihydronaphthalene, m.p.  $54^\circ$  (2),  $48\text{--}50^\circ$

(3) (itself prepd. from naphthol-2 (1:1540) in AcOH + NaOAc soln. with Cl<sub>2</sub> (2) (3)), by shaking with satd. soln. of HCl gas in AcOH for 2-3 min. (2) (3) see indic. refs.; from 1,1,3,4-tetrachloro-2-keto-1,2,3,4-tetrahydronaphthalene [Beil. VII-371] by partial reduction with SnCl<sub>2</sub> in AcOH (poor yield) see (1); from 1-chloronaphthol-2 (3:1700) with SO<sub>2</sub>Cl<sub>2</sub> at ord. temp. (4) (note that this prepn. undoubtedly involves intermediate formn. of 1,1-dichloro-2-keto-1,2-dihydroonaphthalene (above) (2)) see indic. refs.; from 1,4,5-trichloronaphthol-2 [Beil. VI-650] by partial reduction with Na/Hg see (4).]

$\bar{C}$  in AcOH with Cl<sub>2</sub> gives (1) 1,1,4-trichloro-2-keto-1,2-dihydronaphthalene [Beil. VII-386], m.p. 86-87°, together with other oily by-products.]

$\bar{C}$  with SnCl<sub>2</sub>/AcOH/HCl in s.t. at 100° for 8 hrs. gives (72% yield (2)) (3) 4-chloronaphthol-2 (3:3045), m.p. 103-104°.

$\bar{C}$  in AcOH mixed with conc. HNO<sub>3</sub> (*D* = 1.42) and cautiously warmed until the liq. shows intense red color, then poured into nq., yields (1) 4-chloro-3-nitronaphthoquinone-1,2 [Beil. VII-724], red ndls. from AcOH, m.p. 184° (1).

$\bar{C}$  with aq. alc. Na<sub>2</sub>SO<sub>3</sub> boiled 72 hrs. gives in poor yield (2) 4-chloronaphthol-2-sulfonic acid-1, cryst. from aq. with  $\frac{1}{2}$  H<sub>2</sub>O (not lost at 100° in vac.); note that this prod. on hydrolysis with H<sub>2</sub>SO<sub>4</sub> gives (91% yield (2)) 4-chloronaphthol-2 (3:3045), m.p. 103-104°.

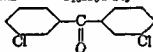
⑤ 1,4-Dichloro-2-naphthyl acetate: m.p. 90-91° (1). [From  $\bar{C}$  with AcCl (1).]

3:3840-3:3860 (2) Burton, *J. Chem. Soc.* 1945, 280-283. (1930). (4) Armstrong, Rossiter, *Chem.*

### 3:3860 3,3'-DICHLOROBENZOPHENONE (Di-(*m*-chlorophenyl) ketone)



Beil. S.N. 652



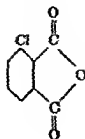
M.P. 123.8-124.9° (1) B.P. 160-166° at 2 mm. (1)

[For prepn. of  $\bar{C}$  from *m*-chlorobromobenzene [Beil. V-209, V<sub>1</sub>-(115), V<sub>2</sub>-(161)] (2) via conversion to *m*-chlorophenyl MgBr (cf. (3)) and reaction with *m*-chlorobenzonitrile [Beil. IX-339] (4), followed by hydrolysis (77% yield), see (1).]

⑥ 3,3'-Dichlorobenzophenone 2,4-dinitrophenylhydrazone: m.p. 235-238° (1).

3:3860 (1) Haller, Bartlett, Drake, Newmann, Cristol, et al., *J. Am. Chem. Soc.* 67, 1600-1602 (1945). (2) Hartwell, *Org. Syntheses* 24, 22-24 (Note 5) (1944). (3) Hein, Retter, *Ber.* 71, 1968 (1938). (4) Korczynski, Fandrich, *Compt. rend.* 183, 421-423 (1926); *Cent.* 1926, II 1853; *C.A.* 21, 77 (1927).

## 3:3900 3-CHLOROPHTHALIC ANHYDRIDE

 $C_8H_5O_3Cl$ Beil. XVII - 482  
XVII<sub>1</sub>—

M.P. 126°	(1)
124.5-125.5°	(2)
123°	(3)
122°	(4) (5)

[See also 3-chlorophthalic acid (3:4820).]

[For prepn. of  $\bar{C}$  from 3-chlorophthalic acid (3:4820) by distn. see (4) (2); from 3-nitrophthalic anhydride [Beil. XVII-486, XVII<sub>1</sub>-(256)] by htg. with  $PCl_3$  in s.t. 6 hrs. at 175° (5) or 9 hrs. at 220° (60% yield (1)) or with  $Cl_2$  at 240° (6) see indic. refs.; from phthalic anhydride (1:0725) with  $Cl_2$  at 240° in pres. of Fe or Fe salts see (7).]

$\bar{C}$  with  $Cl_2$  in fuming  $H_2SO_4$  in pres. of  $I_2$  gives (8) a mixt. contg. 3 pts. 3,6-dichlorophthalic anhydride (3:4860), m.p. 194° cor., and 1 pt. 3,4-dichlorophthalic anhydride (3:3695), m.p. 120-121°, b.p. 320°.]

[The neutral dimethyl and diethyl esters corresp. to  $\bar{C}$  are unreported; ethyl hydrogen 3-chlorophthalate has m.p. 118-119° (3).]

$\bar{C}$  with  $PCl_5$  (3) or with  $SOCl_2$  +  $ZnCl_2$  in s.t. at 200-240° (9) yields 3-chlorophthaloyl (di)chloride, b.p. 169-171° at 10 mm. (3).]

$\bar{C}$  with urea on fusion at 170° gives (3) 3-chlorophthalimide, cryst. from AcOH, m.p. 233° (3), 236° (15). —  $\bar{C}$  with 1 mole aniline htd. at 200-220° until no more steam is evolved (14) or  $\bar{C}$  with 1 mole aniline in boilg. AcOH (14) gives quant. yield 3-chlorophthalanil (N-phenyl-3-chlorophthalimide), pale cream-colored ndls. from AcOH, m.p. 189-190° (14);  $\bar{C}$  similarly treated with p-toluidine gives (80-90% yield (14)) N-(p-tolyl)-3-chlorophthalimide, colorless ndls. from AcOH, m.p. 160.5° (14).

$\bar{C}$  with pyrocatechol (1:1520) +  $AlCl_3$  + NaCl htd. at 130-138° gives (10) an intermediate prod. (presumably 3-chloro-2-(o,m-dihydroxybenzoyl)benzoic acid), yel. cryst. from AcOH, m.p. 187° (10), which with conc.  $H_2SO_4$  yields (10) 8-chloro-1,2-dihydroxyanthraquinone (5-chlorohystazarin), yel. cryst. from pyridine, m.p. 187° (diacetate, m.p. 193° (10)). —  $\bar{C}$  with hydroquinone (1:1590) +  $AlCl_3$  + NaCl htd. at 200-220° for 40-50 min. yields (11) 8-chloro-1,4-dihydroxyanthraquinone (5-chloroquinizarin), red cryst. from xylene, m.p. 213° (diacetate, m.p. 205°, dimethyl ether, m.p. 208° (11)).]

$\bar{C}$  with  $C_6H_4$  +  $AlCl_3$  yields (12) 6-(37)-chloro-2-(benzoyl)benzoic acid, m.p. 233.5°, which with conc.  $H_2SO_4$  for 4 hrs. at 95° gives (59% yield (12)) 1-chloroanthraquinone (3:4180), m.p. 162° (12). —  $\bar{C}$  with p-xylene +  $AlCl_3$  gives (81% yield (13)) 6-(37)-chloro-2-(2,5-dimethylbenzoyl)benzoic acid, pr. from AcOH, m.p. 215°, which on warming with 9 pts. fuming  $H_2SO_4$  (10%  $SO_3$ ) gives (96% yield (13)) 1-chloro-5,8-dimethylanthraquinone, yel. ndls. from AcOH, m.p. 186°.]

$\bar{C}$  on boilg. with dil.  $HCl$  (1) or  $\bar{C}$  on saponification with standard alk. (Sap. Eq. = 91.3) followed by acidifn. gives 3-chlorophthalic acid (3:4820) q.v.

3:3900 (1) Smith, *J. Chem. Soc.* 1933, 1613-1614. (2) Guareschi, *Gazz. chim. ital.* 17, 122 (1887). (3) von Braun, *Lärbig, Knecht, Ber.* 56, 2335 (1923). (4) Kröger, *Ber.* 18, 1729 (1885). (5) Bogert, *Bornschek, J. Am. Chem. Soc.* 23, 751-752 (1901). (6) Imperial Chem. Ind., Ltd., *Flaw, Thomas, Brit.* 357,165, Oct. 15, 1931; *Cent.* 1931, II 3663. (7) Dvornikoff (to Monsanto

Chem. Co.), U.S. 2,028,353, Jan. 21, 1936; *Cent.* 1936, I 2530; *C.A.* 30, 1394 (1936). (8) Villiger, *Ber.* 42, 3549 (1909). (9) Kyrides (to Monsanto Chem. Co.), U.S. 1,951,364, March 20, 1934; *Cent.* 1934, II 333. (10) Waldmann (to I.G.), *Ger.* 642,719, March 12, 1937; *Cent.* 1937, I 5048-5049; *C.A.* 31, 6261 (1937).

(11) Waldmann, *J. prakt. Chem.* (2) 130, 100 (1931). (12) Dougherty, Gleason, *J. Am. Chem. Soc.* 52, 1024-1027 (1930). (13) Mayer, *Heil. Ber.* 55, 2163 (1922). (14) Marriott, Robinson, *J. Chem. Soc.* 1939, 136-137. (15) Drew, Pearman, *J. Chem. Soc.* 1937, 31.

## 3:3925 7-CHLORONAPHTHOL-2

 $C_{10}H_7OCl$ 

Beil. VI - 649

VI—

VI<sub>2</sub>-(603)

M.P. 126.5° (1)

White lfts. from lgr.

[For prepn. of  $\bar{C}$  from 7-hydrazinonaphthol-2 [Beil. XV-613] by treatment of its soln. in dil. HCl with  $CuSO_4$  (19% yield) see (1).]

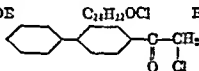
[ $\bar{C}$  (as sodium salt) treated with  $CO_2$  at 230-250° and 45 atm. press. yields (2) 7-chloro-2-hydroxynaphthol acid-3, yellowish lfts. from AcOH, m.p. 277-278° (2).]

⑦ 7-Chloro-2-naphthyl acetate: lfts. from toluene, m.p. 104.5° (1). [From  $\bar{C}$  on refluxing with acetyl chloride (1).]

3:3925 (1) Fransen, Deibel, *J. prakt. Chem.* (2) 78, 154 (1875). (2) Lange, Larc, Jacobs (to I.G.), *Ger.* 564,128, Nov. 14, 1932; *Cent.* 1933, II 446.

## 3:3934 p-PHENYLPHENACYL CHLORIDE

(*p*-Chloro-*p*-phenylacetophenone;  
chloromethyl *p*-xenyl ketone;  
4-(chloroacetyl)biphenyl)

 $C_{14}H_{11}OCl$ 

Beil. VII - 443

VII—

M.P. 126-127° (1)

122-123° (2) (3)

Pale yel. ndls. from dil. alc.

[For prepn. of  $\bar{C}$  from biphenyl (1:7175) with chloroacetyl chloride (3:5235) +  $AlCl_3$  (41% yield (2)) (3), or with chloroacetic acid anhydride (3:0730) +  $AlCl_3$  (77% yield (2)), see indic. refs.]

[ $\bar{C}$  with chloroacetyl chloride (3:5235) +  $AlCl_3$  gives (52% yield (2)) 4,4'-bis-(chloroacetyl)biphenyl, ndls. from di-*n*-propyl ketone or cyclohexanone, m.p. 228-229° (2), 226-227° (4); note that this prod. with excess piperidine yields (4) 4,4'-bis-(piperidinoacetyl)biphenyl, brownish yel. pdr. from acetone, m.p. 143-144° (4).]

[ $\bar{C}$  with piperidine has not been directly reported but should yield 4-(piperidinoacetyl)biphenyl, ndls. from abs. alc., m.p. 93-94° (4), as has been demonstrated for the analogous *p*-phenylphenacetyl bromide.]

$\bar{C}$  with salts of acids should yield the corresp. *p*-phenylphenacetyl esters (for table of examples see Vol. I, p. 652) although the usual reagt. for this purpose is the more common

$\bar{C}$  is oxidized (3) to *p*-phenylbenzoic acid

3:3934 (1) Eastman Kodak Co., List No. 34 (1944). (2) Silver, Lowy, *J. Am. Chem. Soc.* 56, 2429-2430 (1934). (3) Collet, *Bull. soc. chim.* (3) 17, 510 (1897). (4) Carpenter, Turner, *J. Chem. Soc.* 1934, 872.

## 3:3945 5-CHLORONAPHTHOL-2



Beil. VI - 649

VI<sub>1</sub>—VI<sub>2</sub>—

M.P. 128° u.c. (1)

Ndls; sol. alc., AcOH,  $C_6H_6$ ,  $CS_2$ . — Sublimes; volatile with steam.[For prepn. of  $\bar{C}$  from salts of 2-hydroxynaphthalenesulfonic acid-5 [Beil. XI-282] by htg. with  $PCl_5$ , then distilling with steam, see (1).]3:3945 (1) Claus, *J. prakt. Chem.* (2) 39, 317 (1869).

## 3:3952 4,6-DICHLORO-3-HYDROXY-BENZALDEHYDE

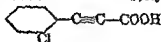


Beil. VIII —

VIII<sub>1</sub>-(526)

M.P. 130° (1)

129° (2)

Fairly eas. sol. hot aq.; eas. sol.  $C_6H_6$ , alc.; insol. lgr. — Volatile with steam.  $\bar{C}$  has very pronounced stermutatory props and also attacks moist skin producing painful blisters (2).[For prepn. of  $\bar{C}$  from 4,6-dichloro-3-methylphenol (3:1745) via conv. to bis-(4,6-dichloro-3-methylphenyl) carbonate, chlorination of latter, and subsequent alk. hydrol. of the chlorination prod. see (1); for formn. (in small amt. together with much 2,6 isomer) from 6-chloro-3-hydroxybenzaldehyde (3:3350) or from *m*-hydroxybenzaldehyde (1:0055) in AcOH with  $Cl_2$  see (2) ] $\bar{C}$  in 4 pts. AcOH + 1 pt. aq. treated grad. with 1 pt. conc.  $HNO_3$  ( $D \approx 1.4$ ) yields (1) 4,6-dichloro-2-nitro-3-hydroxybenzaldehyde, m.p. 157° (1); this prod with acetone and alk. yields (1) the corresp. indigoid, viz., 4,4,6,6-tetrachloro-7,7-dihydroxyindigo.— 4,6-Dichloro-3-methoxybenzaldehyde: ndls. from  $C_6H_6$ , m.p. 117° (1).3:3952 (1) Friedländer, Schenck, *Ber.* 47, 3048, 3051 (1914). (2) Hodgson, Beard, *J. Chem. Soc.* 1926, 148-149, 152.3:3956 *o*-CHLOROPHENYLPROPIOLIC ACID

Beil. S.N. 950

M.P. 131-132° (1) (2)

131° (3)

Cryst. from 50% AcOH or  $C_6H_6$ .[For prepn. of  $\bar{C}$  from *o*-chlorobenzaldehyde (3:6410) by conversion through *o*-chlorocinnamic acid to ethyl *o*-chlorocinnamate, thence by addn. of  $Br_2$  to give ethyl  $\beta$ -(*o*-chlorophenyl)- $\alpha,\beta$ -dibromopropionate, followed by elimination of 2 HBr and saponification (or vice versa) with alc. KOH, and final acidification (68% yield (1)) (2) cf. (3), see indic. refs.] $\bar{C}$  suspended in aq., treated with  $NaHCO_3$  +  $CuCl_2$ , and steam-distilled (1) or  $\bar{C}$  with  $Cu(OAc)_2$  (2) loses  $CO_2$  giving (66% yield) *o*-chlorophenylacetylene (3:9497).3:3956 (1) Bergmann, Bondi, *Ber.* 66, 282-283 (1933). (2) Otto, *J. Am. Chem. Soc.* 56, 1393-1394 (1934). (3) Wilson, Wenzke, *J. Am. Chem. Soc.* 57, 1265-1267 (1935).



## 3:3960 5-CHLORONAPHTHOL-1

 $C_{10}H_7OCl$ 

Beil. VI - 612

VI<sub>1</sub>—VI<sub>2</sub>—

M.P. 131.5° (1)

Ndls. from aq., lfts. from  $CS_2$ ; spar. sol. aq. —  $\bar{C}$  has characteristic odor.[For prepn. of  $\bar{C}$  from  $\gamma$ -(2-chlorophenyl)paraconic acid [Beil. XVIII-421] on rapid distn. see (1).][For condensation of  $\bar{C}$  with subst. isatin chlorides in prepn. of indigoid dyes see (2).] $\bar{C}$  dis. in aq. alk. and this soln. couples (1) with diazonium salts yielding azo dyestuffs $\bar{C}$  with aq.  $FeCl_3$  gives a yellowish-white ppt. unchanged on stdg.;  $\bar{C}$  with  $Ca(OCl)_2$  soln. gives a pale violet ppt. (1). $\bar{C}$  (1 mole) in  $CHCl_3$  on mixing with  $PhOH$  (1 mole) in  $CHCl_3$  gives (1) ppt. of addn. cpd.,  $\bar{C}.PhOH$ , orange ndls. from hot  $CHCl_3$ , m.p. 160° (1).⑤ 5-Chloro-1-naphthyl acetate: lfts. from alc., m.p. 53° (1). [From  $\bar{C}$  on protracted boilg. with  $AcCl$  (1)]3:3960 (1) Erdmann, Kirchhoff, *Ann.* 247, 372-374 (1888). (2) I.G., Brit. 318,107, Oct. 23, 1929; *Cent.* 1930, I 1383.3:3965 TETRACHLOROBENZO-  
QUINONE-1,2  
(Tetrachloro-o-quinone) $C_6O_2Cl_4$ 

Beil. VII - 602

VII<sub>1</sub>-(338)

M.P. 133° (1)  
 131-132° (2)  
 130° (4) (7)  
 129-130° (3)  
 129° (11)

[See also tetrachloropyrocatechol (3:4875).]

Red cryst. pdr. (1), cryst. from dil.  $AcOH$  (2).[For prepn. of  $\bar{C}$  from tetrachloropyrocatechol (3:1520) by oxidn. with fuming  $HNO_3$  in  $AcOH$  (81% yield (1) (2) (3) (4) (5) (6) see indic. refs.; from pyrocatechol (1:1520) (2) (3) or pyrocatecholsulfonic acid (7) with  $Cl_2$  in  $AcOH$  see indic. refs.; from tetrachloropyrocatechol monomethyl ether (tetrachloroguaiacol) (8) or from tetrachloropyrocatechol dimethyl ether (tetrachloroveratrole) (8) by oxidn. with  $HNO_3$  see indic. refs.][ $\bar{C}$  adds 1 mole  $Cl_2$  yielding (9) hexachlorocyclohexene-3-dione-1,2 [Beil. VII-575] q.v. which on reduction with  $SnCl_2$  in  $AcOH$  (3) gives tetrachloropyrocatechol (3:4875).][ $\bar{C}$  with  $PCl_5$  (2 moles) htd. in s.t. at 200-210° for  $\frac{1}{2}$  hr. gives (10) hexachlorobenzene (3:4939) and other products.][For complex behavior of  $\bar{C}$  on htg. with aq., with cold alcs., or with aniline see Beil. VII-602, VII<sub>1</sub>-(338).] $\bar{C}$  forms addn. cpds. with many hydrocarbons [e.g.,  $\bar{C}$  with benzene gives  $\bar{C}.3C_6H_6$ , m.p. 37-42° (11);  $\bar{C}$  with toluene gives  $\bar{C}.C_7H_8$ , m.p. 45-50° (11);  $\bar{C}$  with hexamethylbenzene (1:7265) gives  $\bar{C}.C_{12}H_{18}$ , greenish black ndls. from  $AcOH$ , m.p. 140-143° (11).] $\bar{C}$  with equiv. tetrachloropyrocatechol (3:4875) in least possible hot  $CHCl_3$  gives on

cooling the corresp. quinhydrone (6). — (For study of oxidn.-reductn. potential of system  $\bar{C}$ /tetrachloropyrocatechol see (4) (5).)

3:3965 (1) Jackson, MacLaurin, *Am. Chem. J.* **37**, 11-12 (1907). (2) Zincke, *Ber.* **20**, 1779 (1887). (3) Zincke, Küster, *Ber.* **21**, 2729-2730 (1888). (4) Conant, Fieser, *J. Am. Chem. Soc.* **46**, 1873, 1875 (1924). (5) Kvalnes, *J. Am. Chem. Soc.* **56**, 2487-2489 (1934). (6) Jackson, Carleton, *Am. Chem. J.* **39**, 497 (1909). (7) Datta, Bhounik, *J. Am. Chem. Soc.* **43**, 313 (1921). (8) Cousin, *Compt. rend.* **123**, 967 (1899). (9) Zincke, Küster, *Ber.* **22**, 487 (1889). (10) Zincke, Küster, *Ber.* **24**, 927-928 (1891). (11) Pfeiffer, *Ann.* **412**, 294-296 (1916).

3:3986 5,7-DICHLORONAPHTHOL-1



$C_{10}H_6OCl_2$

Beil. VI - 612  
VI<sub>1</sub>—

M.P. 132° (1) (2)

Pale yel. pr. (from  $CS_2$ ) (1) (2). — Somewhat sol. hot aq.

[For prepn from  $\gamma$ -(2,4-dichlorophenyl)paraconic acid {Beil. XVIII-421} by distn. see (2) ]

$\bar{C}$  with  $FeCl_3$  gives a white ppt. which on htg. with excess reagt. colors violet (2).

$\bar{C}$  in dil. alk. soln. couples with diazotized naphthionic ac. (1-aminonaphthalenesulfonic acid-4) giving intense purple color (2).

$\bar{C}$  on distn. with Zn dust yields naphthalene (1:7200) (2) (1).

⑤ 5,7-Dichloro-1-naphthyl acetate: from  $\bar{C}$  on protracted refluxing with 4 pts.  $AcCl$ ; pr. (from  $CHCl_3$  + 1gr.), m p. 110° (2).

3:3985 (1) Erdmann, Schwechten, *Ber.* **21**, 3444 (1888). (2) Erdmann, Schwechten, *Ann.* **215**, 284-285 (1893).

# CHAPTER X

## DIVISION A. SOLIDS

(3:4000-3:4499)

3:4000 4-CHLORONAPHTHO-  
QUINONE-1,2



$C_{10}H_5O_2Cl$

Beil. S.N. 674

M.P. 132-136° dec. (1)  
[188° (2) see text]

Orange-red ndls. from  $C_6H_6$  by addn. of lgr.;  $\bar{C}$  could not be further purified by recrystallization since some decompn. always occurred (1).

[For prepn. of  $\bar{C}$  from 1,4-dichloronaphthol-2 (3:3840) by conversion (59% yield) with  $HNO_3$  in  $AcOH$  to 1,4-dichloro-1-nitro-2-keto-dihydronaphthalene, followed by subsequent elimination of  $NOCl$  by boiling with  $C_6H_6$  (80% yield), see (1). — Note that the prod. of m.p. 188°, maroon ndls. from alc., obtd. (2) from 4-chloro-1,2-diaminonaphthalene (4-chloronaphthylenediamine-1,2) by air oxidn., is regarded as  $\bar{C}$ ; this discrepancy is unexplained.]

$\bar{C}$  on reductive acetylation with  $Ac_2O + NaOAc + Zn$  dust loses its halogen atom giving (60% yield (1)) 1,2,4-triacetoxynaphthalene [Beil. VI-1183], m.p. 134-135° (1).

[ $\bar{C}$  with 2,3-dimethylbutadiene (1:8050) in specially purified  $CHCl_3$  in s.t. at 100° in dark for 72 hrs. undergoes a Diels-Alder type addition only very slowly (1); no intermediate addn. prod. could be isolated (difference from the isomeric 3-chloronaphthoquinone-1,2 (3:4704)), but on stdg. the soln. slowly deposits (15% yield (1)) 2,3-dimethylphenanthraquinone, m.p. 237-238° u.c.; 242-243° cor. (1).]

— 4-Chloronaphthoquinone-1,2-oxime-2 (4-chloro-2-nitrosonaphthol-1) [Beil. VII- (385)]: pale yel. ndls., m.p. 157°. [Prepd. indirectly.]

3:4000 (1) Fieser, Dunn, *J. Am. Chem. Soc.* 59, 1019-1020 (1937). (2) Hodgson, Elliott, *J. Chem. Soc.* 1935, 1853.

3:4005 1,4,5-TRICHLORONAPHTHALENE



$C_{10}H_5Cl_3$

Beil. V - 545

$V_1$ —

$V_2$ -(446)

M.P. 133° (1)  
131° (2) (3) (4)  
129° u.c. (3)

Ndls. from alc. in which  $\bar{C}$  is spar. sol. — Volatile with superheated (3) steam.

[For formn. of  $\bar{C}$  from sodium 1,5-dinitronaphthalenesulfonate-4 (1) with  $HCl + NaClO_3$

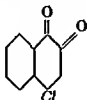


# CHAPTER X

## DIVISION A. SOLIDS

(3:4000-3:4490)

3:4000 4-CHLORONAPHTHO-  
QUINONE-1,2



$C_{10}H_7O_2Cl$

Beil. S.N. 674

M.P. 132-136° dec. (1)  
[188° (2) see text]

Orange-red ndls. from  $C_6H_6$  by addn. of lgr.;  $\bar{C}$  could not be further purified by recrystallization since some decompn. always occurred (1).

[For propn. of  $\bar{C}$  from 1,4-dichloronaphthol-2 (3:3840) by conversion (59% yield) with  $HNO_3$  in AcOH to 1,4-dichloro-1-nitro-2-keto-dihydronaphthalene, followed by subsequent elimination of  $NOCl$  by boiling with  $C_6H_6$  (80% yield), see (1). — Note that the prod. of m.p. 188°, maroon ndls. from alc., obt'd. (2) from 4-chloro-1,2-diaminonaphthalene (4-chloronaphthylendiamine-1,2) by air oxidn., is regarded as  $\bar{C}$ ; this discrepancy is unexplained.]

$\bar{C}$  on reductive acetylation with  $Ac_2O + NaOAc + Zn$  dust loses its halogen atom giving (60% yield (1)) 1,2,4-triacetoxynaphthalene [Beil. VI-1133], m.p. 134-135° (1).

[ $\bar{C}$  with 2,3-dimethylbutadiene (1:8050) in specially purified  $CHCl_3$  in s.t. at 100° in dark for 72 hrs. undergoes a Diels-Alder type addition only very slowly (1); no intermediate addn. prod. could be isolated (difference from the isomeric 3-chloronaphthoquinone-1,2 (3:4704)), but on stdg. the soln. slowly deposits (15% yield (1)) 2,3-dimethylphenanthraquinone, m.p. 237-238° u.c.; 242-243° cor. (1).]

— 4-Chloronaphthoquinone-1,2-oxime-2 (4-chloro-2-nitrosonaphthol-1) [Beil. VII- (385)]: pale yel. ndls., m.p. 157°. [Prepd. indirectly.]

3:4000 (1) Fieser, Dunn, *J. Am. Chem. Soc.* 59, 1019-1020 (1937). (2) Hodgson, Elliott, *J. Chem. Soc.* 1935, 1853.

3:4005 1,4,5-TRICHLORONAPHTHALENE



$C_{10}H_5Cl_3$

Beil. V - 545

V<sub>1</sub>—

V<sub>2</sub>-(446)

M.P. 133° (1)  
131° (2) (3) (4)  
129° u.c. (3)

Ndls. from alc. in which  $\bar{C}$  is spar. sol. — Volatile with superheated (3) steam. [For formn. of  $\bar{C}$  from sodium 1,5-dinitronaphthalenesulfonate-4 (1) with  $HCl + NaClO_2$

see (1); for prepn. of C from 1,5-dichloro-4-nitronaphthalene [Beil. V-556] (3), from 1,4-dichloro-5-nitronaphthalene [Beil. V-556, V<sub>1</sub>-(264)] (4) (3), from 4-chloro-1,5-dinitronaphthalene [Beil. V-561] (3), from 1-chloro-4,5-dinitronaphthalene [Beil. V-561] (3), from 4,5-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-162] (5), from 4-chloro-5-nitronaphthalenesulfonyl chloride-1 [Beil. XI-169] (6), from 1-chloro-5-nitronaphthalenesulfonyl chloride-4 [Beil. XI-170] (6), from 5-chloro-4-nitronaphthalenesulfonyl chloride-1 [Beil. XI-170] (6), from 1-chloro-4-nitronaphthalenesulfonyl chloride-5 [Beil. XI-170] (6), or from 4-chloronaphthalene-1,5-bis-(sulfonyl chloride) [Beil. XI-213] (7) (2), each with  $\text{PCl}_5$  as directed, see indic. refs.]

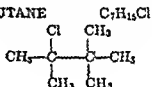
[C treated with  $\text{ClSO}_3\text{H}$  in  $\text{CS}_2$  and reactn. prod. conv. to salts as directed (2) yields a mixt. of two sulfonates, viz., one derived from 1,4,5-trichloronaphthalenesulfonic acid-7 (corresp. sulfonyl chloride, m.p.  $118^\circ$  (2)) and the other derived from 1,4,5-trichloronaphthalenesulfonic acid-X (corresp. sulfonyl chloride, m.p.  $178^\circ$  (2)).]

[C on oxidn. with dil.  $\text{HNO}_3$  in s.t. yields (3) a dichloro acid, presumably 3,6-dichlorophthalic acid (3:4870).]

3:4095 (1) Friedländer, Karamessinis, Schenk, *Ber.* 53, 47 (1922). (2) Turner, Wynne, *J. Chem. Soc.* 1941, 247, 254-255 (3) Atterberg, *Ber.* 9, 1187, 1733-1734 (1870). (4) Widman, *Bull. soc. chim.* (2), 28, 511 (1877). (5) Armstrong, Wynne, *Chem. News* 61, 273 (1890). (6) Cleve, *Chem. Ztg.* 17, 398 (1893). (7) Armstrong, Wynne, *Chem. News* 62, 163 (1890).

## 3:4020 3-CHLORO-2,2,3-TRIMETHYLBUTANE

(*ter*-Butyl-dimethyl-carbinyl chloride)



**Bell. I - 158**

11-60

10

M.P. 136° (1)

133<sup>a</sup> (4)

129° in s.t. (2)

123° (31)

150 101

Colorless cryst with camphoraceous odor; extremely volatile and readily sublimes; insol. aq. and volatile with steam; purified by sublimation or crystallization from boil. MeOH.

(For prepn. of **5** from 2,2,3-trimethylbutanol (207), **12**-(447)) (**3**) or its hydro-... (3.7065) (46% ... with ter-... seconds (18% yield) see (**4**))

C with all cold (3).

with  $\text{O}_2$  and subsequent hydrolysis yields (2) 2,2,3-trimethylbutanol-2, m.p.  $80^\circ$  (2).

$\bar{C}$  converted to  $RMgCl$  and the latter treated with  $CO_2$  yields (2) *ter*-butyl-methylacetic acid [ $BeI$  II<sub>2</sub>-(150)], m p  $80^\circ$  (2)

3:4020 {1} Butlerow, *Ann.* **177**, 183-184 (1875). {2} Richard, *Ann. chim.* (8) **21**, 356-358 (1910).  
{3} Henry, *Compt. rend.* **142**, 1024 (1906); *Rec. trav. chim.* **26**, 104 (1907). {4} Bartlett, Condon,  
Schneider, *J. Am. Chem. Soc.* **66**, 1533, 1537 (1944).

## 3:4030 2,4,6-TRICHLOROPHLOGRUCINOL



$C_6H_3O_3Cl_3$  Beil. VI - 1104  
VI<sub>1</sub>—  
VI<sub>2</sub>—

M.P. 136° u.c. (1)  
134° (2)  
132-133° (3)

Cryst. from abs. alc. — Note that from aq.  $\bar{C}$  cryst. as a trihydrate (1), but on htg. this hydrate loses aq. before melting (2); note also that  $\bar{C}$  on recrystn from toluene gives a solvated prod., m.p. 108-109° (1). [For study of crystallography of  $\bar{C}$  see (4).]

$\bar{C}$  is alm. insol. aq. or cold  $C_6H_6$ ; sol. alc. —  $\bar{C}$  readily sublimes.

[For prepn. of  $\bar{C}$  from phloroglucinol (1,3,5-trihydroxybenzene) (1:1620) with  $Cl_2$  in  $CCl_4$  (crude yield 76% (1)) or in AcOH (5) see indic. refs.; note that attempts (6) (7) to prepare  $\bar{C}$  from phloroglucinol (1:1620) with  $Cl_2$  in aq. soln. were not effective owing to further decomp. of the prod. into dichloroacetic acid (3:6208) and/or the tetrahydrate of sym.-tetrachloroacetone (3:6050) cf. (1).]

[For formn. of  $\bar{C}$  from phloroglucinol (1:1620) with  $SO_2Cl_2$  in dry ether see (3).]

[For formn. of  $\bar{C}$  from hexachlorocyclohexanetrioo-1,3,5 ("hexachlorophloroglucinol") [Beil. VII-854, VII<sub>1</sub>-(469)] by reduction with  $SnCl_2$  or KI see (7).]

$\bar{C}$  dis. in hot conc. HCl from which on cooling it separates in fine ndls.;  $\bar{C}$  with warm dil.  $HNO_3$  is decomposed with formn. of oxalic acid (1:0445);  $\bar{C}$  with conc.  $H_2SO_4$  dissolves unchanged on gentle warming, but on contd. htg. HCl is evolved and soln. turns deep sage-green (1).

$\bar{C}$  dissolves in aq. alk. but is reprecip. unchanged upon acidification; note, however, that alk. soln. of  $\bar{C}$  on stdg. in air develops a purple color (1).

[ $\bar{C}$  in AcOH added to excess  $Br_2$ /aq. undergoes ring cleavage with formn. of 1,1,3,5,5-pentabromo-1,3,5-trichloropentanedione-1,4 [Beil. I-786], colorless cryst. from pet. ether, m.p. 93-95°, to a turbid liq. becoming clear at 98° (8).]

— 2,4,6-Trichlorophloroglucinol trimethyl ether: ndls. from alc., m.p. 130-131° (9). [Prepd. indirectly (9)]

— 2,4,6-Trichlorophloroglucinol triacetate: lfts. from dil. AcOH, m.p. 167-168° (7). [From  $\bar{C}$  with large excess  $AcCl$  at 100° (7).]

3:4030 (1) Webster, *J. Chem. Soc.* **47**, 423-426 (1885). (2) Zincke, Kegel, *Ber.* **23**, 1731-1732 (1890). (3) Peratoner, Finocchiaro, *Gazz. chim. ital.* **24**, I 243-244 (1894). (4) Déverin, *Bull. C.A.* **31**, 4320 (1940). (5) Hazura, Hermann, *Ann.* **155**, 132-134 (1870). Kegel, *Ber.* **23**, 1720-1721 (1890).

(9) Ciamician, Silber, *Ber.* **24**, 2980-2981 (1891).

## 3:4040 2,6-DICHLORONAPHTHALENE



$C_{10}H_8Cl_2$  Beil. V - 544  
V<sub>1</sub>—  
V<sub>2</sub>-(446)

M.P. 136° (1) (2) B.P. 285° u.c. (4)  
135-136° (13)  
135-135.5° u.c. (3)  
135° u.c. (4)  
135° (5) (6) (7)  
(9) (19)

TbIs. from ether +  $C_6H_6$ , ndIs from hot alc., pr. from AcOH. — Spar. sol. alc.; eas. sol. ether,  $C_6H_6$ , or  $CHCl_3$ . — Volatile with steam.

[For prepn. of  $\tilde{C}$  from naphthalene-2,6-bis-(sulfonyl chloride) [Beil. XI-216] (8) (10), from 6-chloronaphthalene-2-sulfonyl chloride [Beil. XI-180] (45% yield (2)) (1) (9), from 6-bromonaphthalene-2-sulfonyl chloride [Beil. XI-184] (11), from salts of 2-hydroxynaphthalenesulfonate-6 [Beil. XI-282, XI-(66)] (59% yield (3)) (4) (5), or from 6-bromonaphthol-2 [Beil. VI-651] (55% yield (12)) with  $PCl_5$  as directed, see indic. refs.; from 6-sulfonaphthylamine-2 [Beil. XIV-760, XIV-(735)] by treatment of corresp. diazonium chloride with  $PCl_5$  in  $POCl_3$  see (13) (14), from 2,6-diammonaphthalene [Beil. XIII-208] via tetrazotization in HCl followed by hlg. with Cu pdr. see (6), from sodium  $\beta$ -naphthalenesulfonate [Beil. XI-171, XI-(38)] with  $KClO_4$  + boilg. dil. HCl (50% yield) see (15).]

[ $\tilde{C}$  in  $CHCl_3$  satd. with  $Cl_2$  gives (9% yield (20)) 1,2,6-trichloronaphthalene (3:2515), m.p. 92°.]

$\tilde{C}$  on oxidn. with dil.  $HNO_3$  ( $D \approx 1.2$ ) in s.t. at 150° (16) or better with dil.  $HNO_3$  ( $D = 1.13$ ) in s.t. at 190-200° (17) yields 4-chlorophthalic acid (3:4390), m.p. 148° u.c. (17). —  $\tilde{C}$  on oxidn. with  $CrO_3$ /AcOH yields (18) 2,6-dichloronaphthoquinone-1,4 [Beil. VII-730], bright yel. ndIs, m.p. 143-149° (18), this cpd. also accompanies (18) the 4-chlorophthalic acid of the same m.p. during  $HNO_3$  oxidn. (above)

[ $\tilde{C}$  on mononitration yields (16) two isomers, one m.p. 139-139.5°, the other m.p. 113.5-114° (16).]

[ $\tilde{C}$  in  $CS_2$  treated with  $ClSO_3H$  yields (19) 2,6-dichloronaphthalenesulfonic acid-4 [Beil. XI-162] (corresp. sulfonyl chloride, m.p. 136°, corresp. sulfonamide, m.p. 260°).]

3:4040 (1) Forsling, *Ber.* 20, 80-81 (1887). (2) Beattie, Whitmore, *J. Am. Chem. Soc.* 55, 1516 (1933). (3) W. Schaeffer, *Sammlung* 7, 41-42 (1887). (4) Claus, *Ber.* 20, 146-147 (1933). (5) Claus,

Arnell, *Bull. soc. chim.* (2) 45, 184 (1886). (10) Armstr.

(11) Sindall, *Chem. News* 60, 58 (1889). (12) Franzen, Stauble, *J. prakt. Chem.* (2) 103, 370 (1921/22). (13) Erdmann, *Ann.* 275, 280 (1893). (14) Nakata, *Ber.* 64, 2067 (1931). (15) Kozlov, Talybov, *J. Gen. Chem. (U.S.S.R.)* 9, 1827-1833 (1939), *C.A.* 34, 4067 (1940). (16) Alén, *Bull. soc. chim.* (2) 36, 434 (1861). (17) Claus, *Ber.* 51, 320 (1882). (18) Claus, Müller, *Ber.* 18, 3073-3074 (1885). (19) Armstrong, Wynne, *Chem. News* 61, 273-275 (1890). (20) Wynne, *J. Chem. Soc.* 1916, 61.

### 3:4052 2,3,6-TRICHLOROHYDROQUINONE

$C_6H_3O_2Cl_3$  Beil. VI - 850  
VI<sub>1</sub>—  
VI<sub>2</sub>-(846)



M.P. 138° (1)  
136° (2)  
134° (3)  
131-132° (16)  
130-132° (13)  
130° (4)

[See also 2,3,5-trichlorobenzoquinone-1,4 (3:4672).]

Colorless shining pr. from aq. rapidly losing their luster in air (3); transparent pr. with 1 mole AcOH from AcOH but solvated AcOH readily lost in air (5).

$\tilde{C}$  at 15° is sol. in 160 pts. aq. (6);  $\tilde{C}$  is spar. sol. cold aq. but eas. sol. hot aq. in which it first melts to an oil (3);  $\tilde{C}$  is eas. sol. alc. or ether.



$\bar{C}$  readily sublimes in lfts. (4); for study of sublimation press. see (7).

[For study of heat of formn. of  $\bar{C}$  see (8); for studies of heat of combustion of  $\bar{C}$  see (5) (9).]

[For detn. of chlorine in  $\bar{C}$  by hydrogenation at elevated temp. see (10); for patent on use of  $\bar{C}$  as vulcanization accelerator see (11).]

### PREPARATION OF $\bar{C}$

From trichlorobenzoquinone. [For prepn. of  $\bar{C}$  from 2,3,5-trichlorobenzoquinone-1,4 (3:4672) by reduction with aq.  $\text{SO}_2$  (3) (4) (6) (12) in ether (1), or from "benzoquinone tetrachloride" (2,3,5,6-tetrachlorocyclohexanedione-1,4) [Beil. VII-557] with aq.  $\text{SO}_2$  (13), see indic. refs.]

From other sources. [For formn. of  $\bar{C}$  (together with other products) from 2,5-dichlorobenzoquinone-1,4 (3:4470) or from 2,6-dichlorobenzoquinone-1,4 (3:3750) with boilg. conc.  $\text{HCl}$  see (14); from  $\text{C}_6\text{H}_8$  with  $\text{KClO}_3 + \text{H}_2\text{SO}_4$  see (16).]

### CHEMICAL BEHAVIOR OF $\bar{C}$

Reduction. [ $\bar{C}$  with  $\text{Na}/\text{Hg}$  in acid soln. is hardly affected and does not (3) give hydroquinone; however, for anal. of  $\bar{C}$  by quant. detn. of chlorine with  $\text{H}_2$  at elev. temp. see (10).]

Oxidation.  $\bar{C}$  on oxidn., e.g., with  $\text{CrO}_3$  at  $0^\circ$  (5), conc.  $\text{HNO}_3$  (4) (3),  $\text{AgNO}_3$  (4), or  $\text{FeCl}_3$  (4), gives 2,3,5-trichlorobenzoquinone-1,4 (3:4672); note, however, that with insufficient oxidizing agent the corresp. quinhydrone (see below) may separate.

[For study of oxidn.-reductn. potential of system  $\bar{C} + 2,3,5$ -trichlorobenzoquinone-1,4 (3:4672) see (2) (17) (18).]

$\bar{C}$  (1 mole) with 2,3,5-trichlorobenzoquinone-1,4 (3:4672) (1 mole) in  $\text{CHCl}_3$  soln. gives on evapn. (2) (19) the corresp. quinhydrone, green-black cryst., m.p.  $114$ – $115^\circ$  (2),  $103^\circ$  (19).

[Note also that  $\bar{C}$  in aq.  $\text{KOH}$  exposed to air first turns green, then red, and finally brown (4), and this soln. on stdg. or boilg. in air gradually separates the corresp. potassium salt of chloranilic acid (3:4970) (3).]

Other reactions of  $\bar{C}$ . [ $\bar{C}$  with  $\text{PCl}_5$  (2 moles) on btg. gives (3) a mixture of pentachlorobenzene (3:2290) and hexachlorobenzene (3:4939).]

— Trichlorohydroquinone dimethyl ether (3,4,5-trichloro-1,4-dimethoxybenzene): unreported.

① Trichlorohydroquinone diethyl ether (3,4,5-trichloro-1,4-diethoxybenzene): ndls. from alc., m.p.  $68.5^\circ$  (3). [From  $\bar{C}$  with  $\text{C}_2\text{H}_5\text{I} + \text{KOH}$  in s.t. (3).]


② Trichlorohydroquinone diacetate: ndls. by sublimation, m.p.  $153^\circ$  (3). [From  $\bar{C}$  with  $\text{AcCl}$  under reflux (3).]

③ Trichlorohydroquinone dibenzoate: ndls. from  $\text{CS}_2$ , m.p.  $174^\circ$  (14). [From  $\bar{C}$  with  $\text{BzCl}$  on btg. (14).]

3:4052 (1) Biltz, Giese, *Ber.* 37, 4017 (1904). (2) Conant, Fieser, *J. Am. Chem. Soc.* 45, 2206–2207 (1923). (3) Graebe, *Ann.* 146, 22–30 (1868). (4) Städeler, *Ann.* 69, 321–326 (1849). (5) Valeur, *Ann. chim.* (7) 21, 496–499 (1900). (6) Stenhouse, *Ann. Suppl.* 6, 218 (1868). (7) A. S. Coolidge, M. S. Coolidge, *J. Am. Chem. Soc.* 49, 100–104 (1927). (8) Sjöström, *Seenskt Kem. Tid.* 48, 121–124 (1936); *Cent.* 1937, I 58; *C.A.* 30, 6634 (1936). (9) Swietoslawski, Starczewska, *J. chim. phys.* 22, 399–401 (1925). (10) ter Meulen, Heslinga, *Rec. trav. chim.* 42, 1093–1096 (1923).

(11) Fisher (to Nautaguet Chem. Co.), French 740,978, Feb. 3, 1933; *Cent.* 1933, I 3134; *C.A.* 27, 2845 (1933). (12) Graebe, *Ann.* 263, 28 (1891). (13) Peratoner, Genco, *Gazz. chim. ital.* 24, II 389–390 (1894). (14) Levy, Schultz, *Ann.* 210, 153–154 (1881). (15) Krafft, *Ber.*

10, 797-800 (1877). (16) Carius, *Ann.* **142**, 129-138 (1867). (17) Conant, *J. Am. Chem. Soc.* **49**, 293-297 (1927). (18) Kvalnes, *J. Am. Chem. Soc.* **56**, 667-670 (1934). (19) Ling, Baker, *J. Chem. Soc.* **63**, 1322-1323 (1893).

**3:4065 3-CHLORO-4-HYDROXYBENZ-ALDEHYDE**   $C_7H_5O_2Cl$  Beil. VIII - 81 VIII<sub>1</sub>—

M.P. 139° cor. (1) B.P. 149-150° at 14 mm. (1)  
132-134° (2)  
127-128° (3)

Ndls. from aq. (1). — Very spar. sol. cold aq., eas. sol. hot aq.; spar. sol.  $CHCl_3$ ; eas. sol. alc., ether (1).

[For prepn. of  $\bar{C}$  from *p*-hydroxybenzaldehyde (1:0060) with  $Cl_2 + CHCl_3$  see (1) (2); from 3-chloro-4-hydroxybenzyl alcohol by htg. with alk. sodium *m*-nitrobenzenesulfonate see (3); from *o*-chlorophenol (3:0255) +  $CH_2O$  under specified circumstances see (4) or with chloral (3:5210) see (5).]

$\bar{C}$  with  $FeCl_3$  gives no coloration (3). —  $\bar{C}$  forms a  $NaHSO_3$  cpd. (3).

$\bar{C}$  in  $EtOAc$  hydrogenated with  $H_2$  at 40 lb./sq. in. for 45 min. in presence of Raney Ni cat. gives (2) 3-chloro-4-hydroxybenzyl alc., cryst. from  $C_6H_6$ , m.p. 127° (2).

③ 3-Chloro-4-hydroxybenzaldehyde: ndls. from aq. or  $CHCl_3$ , m.p. 144-145° (1).


— 3-Chloro-4-hydroxybenzaldehyde phenylhydrazone: unrecorded.

— 3-Chloro-4-hydroxybenzaldehyde *p*-nitrophenylhydrazone: unrecorded.

— 3-Chloro-4-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.

④ 3-Chloro-4-hydroxybenzaldehyde semicarbazone: yel. ndls. from very dil.  $AcOH$ , m.p. 210° dec. (1); 212° (3).

**3:4065** (1) Biltz, *Ber.* **37**, 4031-4034 (1904). (2) Buchler, Brown, Holbert, Fulmer, Parker, *J. Org. Chem.* **6**, 904 (1941). (3) Hanus, *J. prakt. Chem.* **158**, 263 (1911). (4) Geigy and Co., Ger 105,793; *Cent.* 1900, I 623. (5) Haack, Smola, Austrian 151,169, March 25, 1935; *Cent.* 1935, I 439.

**3:4085 2-CHLORO-3-HYDROXYBENZ-ALDEHYDE**   $C_7H_5O_2Cl$  Beil. S.N. 745

M.P. 139.5° (1)  
139-139.5° (3)  
139° cor. (4)

Colorless cryst from dil.  $AcOH$  (1) becoming pale pink on prolonged exposure to air (1) —  $\bar{C}$  has pronounced sternutatory props. (1) (3).

[For prepn. of  $\bar{C}$  from *m*-hydroxybenzaldehyde (1:0055) +  $Cl_2$  (32.6% yield (4)) see (1) (3) (4); for indirect prepn. via 2-nitro-3-hydroxybenzaldehyde, reductn., and appropriate diazo reactns. see (1).]

$\bar{C}$  in 50%  $AcOH$  mononitrated as directed (2) by grad. addn. of  $HNO_3$  ( $D = 1.3$ ) then after a min. poured onto ice gives 100% yield of mixt. of 4-nitro and 6-nitro derivs.; extraction with aq. nt 90° dissolves the latter leaving residue of almost pure 4-nitro deriv.; from the soln. of 6-nitro isomer a little dissolved 4-nitro cpd. is distilled out with steam (2).

4-Nitro-2-chloro-3-hydroxybenzaldehyde: pale yel. ndls. from  $AcOH$ , m.p. 166° (2). [Corresp. oxime, insol. aq., yel. ndls. from alc., m.p. 170° (2); *p*-nitrophenylhydrazone, deep or. ndls. from hot  $AcOH$ , m.p. 291-295° dec. (2); semicarbazone, sulfur-yel. ndls.

from hot alc., m.p. 271–272° dec. (2); methyl ether, colorless ndls. from dil. alc. or dil. AcOH, m.p. 107° (2).]

6-Nitro-2-chloro-3-hydroxybenzaldehyde: colorless ndls. from aq., m.p. 153° (2). [Corresp. oxime, exceedingly sol. in aq. or alc., colorless ndls. from  $\text{CHCl}_3$ , m.p. 175° (2); *p*-nitrophenylhydrazone, or.-red ndls. from hot dil.  $\text{AcOH}$ , m.p. 232-233° (2); semicarbazone, pale yel. ndls. from alc., m.p. 234° dec. (2); methyl ether, colorless ndls. from  $\text{AcOH}$ , m.p. 134° (2).]

$\bar{C}$  in  $\text{CHCl}_3$  treated with  $\text{Br}_2$  in  $\text{CHCl}_3$  as directed (5) gives (86% yield (5)) 4-bromo-2-chloro-3-hydroxybenzaldehyde, cryst. from 50%  $\text{AcOH}$ , m.p.  $139\text{--}140^\circ$  cor. (5). [This deriv. depresses m.p. of  $\bar{C}$  (5).] [4,6-Dibromo-2-chloro-3-hydroxybenzaldehyde has m.p.  $104\text{--}105^\circ$  (5).]

5 with 50% KOH at 60–70° undergoes Cannizzaro reactn. giving (4) 2-chloro-3-hydroxybenzyl alc. (87% theory (4)), cryst. from toluene, m.p. 132° cor. (4), and 2-chloro-3-hydroxybenzoic acid (96% theory (4)) (3:4395), cryst. from *aq.*, m.p. 156° (4).

C in aq. 20% NaOH (1) or aq.  $\text{NaHCO}_3$  (1), treated with  $\text{Me}_2\text{SO}_4$ , yields methyl ether (2-chloro-3-methoxybenzaldehyde), volatile with steam, cryst. from dil. alc., m.p. 56–57° (1). [This ether depresses m.p. of corresp. deriv. (m.p. 52°) of the isomeric 4-chloro-3-hydroxybenzaldehyde (3:3780).] [On oxidn. with alk.  $\text{KMnO}_4$  (1) this methyl ether yields 2-chloro-3-methoxybenzoic ac., m.p. 160° (1).]

⑧ 2-Chloro-3-hydroxybenzaloxime: colorless nlds. from dil. alc., m.p. 140° (l).

— 2-Chloro-3-hydroxybenz aldehyde phenylhydrazone: unrecorded.

① 2-Chloro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazone: or.-red ndls. from hot alc., m.p. 244-245° (1).


— 2-Chloro-3-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.

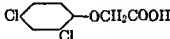
① 2-Chloro-3-hydroxybenzaldehyde semicarbazone: pale yel. nlds., m.p. 236-237° (1).

⑤ **2-Chloro-3-acetoxybenzaldehyde**: rhombic cryst. from alc., m.p. 62° (1).

⑤ 2-Chloro-3-benzoxypyridine: rhombic cryst. from alc., m.p. 88° (1).

3:4085 (1) Hodgson, Beard, *J. Chem. Soc.* 1926, 149-155. (2) Hodgson, Beard, *J. Chem. Soc.* 1926, 2031-2030. (3) Bissell, Kranz (to National Aniline and Chem. Co.), U.S. 1,770,803, Sept. 30, 1930; *Cent.* 1931, II 169; *C.A.* 21, 5768-5769 (1930). (4) Lock, *Monatsh.* 55, 309-311 (1930). (5) Lock, *Monatsh.* 62, 187-188 (1933).

3:4095 2,4-DICHLOROPHENOXYACETIC  $C_8H_6O_3Cl_2$  Bell. S.N. 522  
ACID 



M.P. 140-141° (1)

138° (2)

White odorless cryst. from  $C_6H_6$ ; alm. insol. aq. — Neut. Eq. = 221.0.

[For prepn. of **6** from 2,4-dichlorophenol (**3**:0560) with chloroacetic acid (**3**:1370) in aq. NaOH (87% yield) see (1).]

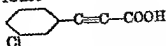
[For general survey of  $\tilde{C}$  as plant hormone see (1) (3) cf. (4); for use of solns. of  $\tilde{C}$  in polyethylene glycols for regulating growth of plants see (5); for use of  $\tilde{C}$  as weed killer see (6).]

314095 (1) ---  
63, 1768 (  
(1942); *C.*  
*C.A.* 37, 14  
(1944). (6.

3:4102 *m*-CHLOROPHENYLPROPIOLIC  
ACID



Beil. S.N. 950



M.P. 140-141° (1)

Cryst. from AcOH.

[For prepn. of  $\bar{\text{C}}$  from *m*-chlorobenzaldehyde (3:6475) by conversion through *m*-chlorocinnamic acid to ethyl *m*-chlorocinnamate, thence by addn. of  $\text{Br}_2$  to give ethyl  $\beta$ -(*m*-chlorophenyl)- $\alpha,\beta$ -dibromopropionate, followed by elimination of 2 HBr and saponification (or vice versa) with alc. KOH, and final acidification (yield not stated), see (1).]

$\bar{\text{C}}$  with  $\text{Cu}(\text{OAc})_2$  loses  $\text{CO}_2$  yielding (1) *m*-chlorophenylacetylene (3:9500) (cf. also under *o*-chlorophenylpropionic acid (3:3956)).

3:4102 (1) Otto, *J. Am. Chem. Soc.* 56, 1393-1394 (1934).

3:4115 1,2,4,5-TETRACHLOROBENZENE



Beil. V - 205

V<sub>1</sub>-(113)V<sub>2</sub>-(157)

M.P. 141°	(1)	B.P. 243-246° cor.	(9)
140-141°	(2)	240°	(5)
139.6-139.9°	(3)	236°	(7)
139.5-140.5°	(4)		
139°	(5) (6) (24)		
138°	(7) (8)		
	(13) (14)		
137-138°	(9) (10)		
137.5°	(11)		
137°	(12) (23)		

Ndls. from ether; cryst. from  $\text{CCl}_4$ ,  $\text{CS}_2$ ,  $\text{C}_6\text{H}_6$  +  $\text{LiOH}$ , or  $\text{C}_6\text{H}_6$  (for studies on crystallographic props. see (2) (8) (5) (15)). — Insol. cold and spar. sol. hot nlc; fairly sol. cold ether,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ , or  $\text{CS}_2$  —  $\bar{\text{C}}$  has penetrating and disagreeable odor. — Sublimes easily.

[For prepn. of  $\bar{\text{C}}$  from 2,4,5-trichloroaniline [Beil. XII-627] (9) or from 2,5-dichlorophenylenediamine [Beil. XIII-118] (16) via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reactn. (64% yield (16)) see indic. refs.; from *p*-dichlorobenzene (3:0950) with  $\text{S}_2\text{Cl}_2$  +  $\text{AlCl}_3$  in  $\text{SO}_2\text{Cl}_2$  (67% yield (1)) (17) or from *o*-dichlorobenzene (3:6055) with  $\text{Cl}_2$  + cat. (18) see indic. refs.]

[For formn. of  $\bar{\text{C}}$  from  $\text{C}_6\text{H}_6$  with  $\text{Cl}_2$  in pres. of  $\text{I}_2$  (5),  $\text{Fe}$  (44% yield (13)), or  $\text{AlCl}_3$  (19), or  $\text{Cu}$  (20), or from chlorobenzene with  $\text{Cl}_2$  +  $\text{Cu}$  (20), or from *o*-dichlorobenzene (3:6055) with  $\text{Cl}_2$  + cat. (18) or  $\text{Al/Hg}$  (21), or from *m*-dichlorobenzene (3:5960) with  $\text{Cl}_2$  +  $\text{Al/Hg}$  (21) or  $\text{AlCl}_3$  (4), or from *p*-dichlorobenzene with  $\text{Cl}_2$  in pres. of  $\text{Fe}$  (39% yield (13)), see indic. refs.; from dry  $\text{C}_6\text{H}_6$  with anhyd.  $\text{AuCl}_3$  (22) or on electrol. in aq.  $\text{HCl}/\text{AcOH}$  soln. see (23); from lower chloro derivs. of  $\text{C}_6\text{H}_6$  with  $\text{FeCl}_3$  see (7); from 2,4,5-trichlorotoluene (3:2100) with  $\text{Cl}_2$  see (21); from benzaldehyde (1:0195) by hlg. with  $\text{SnCl}_4$  see (11)]

[For formn. of  $\bar{\text{C}}$  from 2,5-dichloro-4-nitroaniline on diazotization and treatment with  $\text{Cu}_2\text{Cl}_2$  see (23) (14) (note abnormal replacement of nitro group); from nitrobenzene with  $\text{SO}_2\text{Cl}_2$  +  $\text{N}_2\text{O}_4$  see (10), from resorcinol 4,6-bis-(sulfonyl chloride) or hydroquinone 2,5-

*bis*-(sulfonyl chloride) with  $\text{PCl}_5$  in s.t. at  $180^\circ$  see (12) (26); from 4,6-dichlorobenzene 1,3-*bis*-(sulfonyl chloride) (27) or from 1,3-*bis*-(methylmercapto)benzene-4,6-*bis*-(sulfonyl chloride) (28) with  $\text{SOCl}_2$  at  $170$ – $200^\circ$  see indic. refs.; from 2,5-dichlorobenzene-1,4-*bis*-(sulfonyl chloride) with  $\text{PCl}_5$  in s.t. 4 hrs. at  $180^\circ$  see (6); from 2,3,5,6-tetrachloro-*N*-nitroacetanilide (39) by refluxing in toluene or xylene (other products are also formed) see (39).]

[For behavior of  $\bar{\text{C}}$  with liq.  $\text{Cl}_2$  yielding addn. products see (29); for behavior with  $\text{NH}_3$  at elevated temps. see (30);  $\bar{\text{C}}$  with  $\text{S}_2\text{Cl}_2 + \text{AlCl}_3 + \text{SO}_2\text{Cl}_2$  yields (17) hexachlorobenzene (3:4933).]

[ $\bar{\text{C}}$  htd. with NaOMe as directed yields according to conditions (13) (31) (32) (38) 2,4,5-trichlorophenol (3:1620) or its methyl ether.]

$\bar{\text{C}}$  on mononitration, e.g., on boilg. with 5 pts.  $\text{HNO}_3$  ( $D = 1.52$ ) for  $\frac{1}{2}$  hr. (3) (13) (34), yields 1,2,4,5-tetrachloro-3-nitrobenzene [Beil. V-247], m.p.  $99$ – $100^\circ$  (33) (35),  $99^\circ$  (34) (13),  $98^\circ$  (9), some tetrachlorobenzoquinone (chloranil) (3:4978) (insol. in pet. ether) also being formed (9) (34) (13) (33). [For studies on ebem. of this mononitro cpd. see (36).]

$\bar{\text{C}}$  on dinitration by boilg. 5–6 hrs. with mixt. of 10 pts.  $\text{HNO}_3$  ( $D = 1.52$ ) + 10 pts. fuming  $\text{H}_2\text{SO}_4$  (25%  $\text{SO}_3$ ) gives (71% yield (33)) 1,2,4,5-tetrachloro-3,6-dinitrobenzene, cryst. from  $\text{C}_6\text{H}_6$  by addn. of alc., m.p.  $227$ – $228^\circ$  (33),  $232$ – $233^\circ$  (35).

$\bar{\text{C}}$  with 4 pts. chlorosulfonic acid refluxed for hr. gives (78% yield (37)) hexachlorobenzene (3:4939), m.p.  $218$ – $219^\circ$  u.c. (37).

3:4115 (1) Silberrad, *J. Chem. Soc.* 121, 1020 (1922). (2) Fels, *Z. Krist.* 32, 365 (1900). (3) Dadiou, Pongratz, Kohlrausch, *Monatsh.* 61, 434 (1932). (4) Olivier, *Rec. trav. chim.* 39, 411–413 (1920). (5) Jungfleisch, *Ann. chim.* (4) 15, 277–283 (1868). (6) Gebauer-Fulnegg, Fidor, *Monatsh.* 48, 634 (1927). (7) Thomas, *Compt. rend.* 126, 1212 (1898). (8) Bodewig, *Z. Krist.* 3, 400 (1879). (9) Beilstein, Kurbatow, *Ann.* 192, 236–237 (1876). (10) Battegay, Denivelle, *Bull. soc. chim.* (4) 47, 609 (1930).

(11) Gnehm, Banziger, *Ann.* 296, 67 (1897). (12) Litvay, Riesz, Landau, *Ber.* 62, 1867 (1929). (13) Holleman, *Rec. trav. chim.* 39, 736–737, 745, 749 (1920). (14) Hodgson, *J. Soc. Dyers Colourists* 42, 368 (1926). (15) Groth, *Chem. Krist.* 4, 7 (1917). (16) Schoutissen, *J.*

3,200, March  
7, 1933; *Cent.*  
1028 (1898).  
128, I 2370.  
*J. Am. Chem.*  
24) Beilstein,  
40, 71 (1921).  
*Monatsh.* 35,  
— *chim* 55

*J. Can. (5) 10,*  
(1925). (34)  
*boensis Math.*  
we, Stead, *J.*  
(1940). (38)  
943, 372–373.

## 3:4135 TETRACHLORORESORCINOL

 $\text{C}_6\text{H}_2\text{O}_2\text{Cl}_4$ 

Beil. VI - 820

VI<sub>1</sub>—VI<sub>2</sub>-(819)M.P.  $141^\circ$  (1) $140^\circ$  (2)

Long colorless ndls. from hot aq. — Faintly pleasant phenolic odor. [New comml. prod. (1942) in U.S.A.] — Eas. sol. alc., ether, AcOH,  $C_6H_6$ ; fairly eas. sol. hot aq.; spar. ol. cold aq.

[For prepn. from "hexachlororesorcinol" (3:3470) by reduction with  $SaCl_2$  in AcOH see (1)]

$\bar{C}$  is sol. in aq. alk. (2). —  $\bar{C}$  in aq. soln. gives with  $FeCl_3$  a blue color (2).

$\bar{C}$  in AcOH on treatment with  $Cl_2$  yields "hexachlororesorcinol" (3:3470), m.p. 115°.

⑤ Tetrachlororesorcinol diacetate: m.p. 145° (1), 144° (2). [Note that m.p. of this deriv. is close to that of  $\bar{C}$  and should be tested by method of mixed m.p.'s.]

3:4135 (1) Zincke, Fuchs, *Ber.* 25, 2689-2690 (1892). (2) Fries, Hartmann, *Ber.* 54, 199 (1921).

### 3:4140 2,4-DICHLORO-3-HYDROXYBENZ-ALDEHYDE



$C_7H_3Cl_2O_2$  Beil. S.N. 745

M.P. 141° (1)

Colorless cryst. from AcOH.  $\bar{C}$  has pronounced sternutatory props. and blisters moist skin. — [Note that the m.p. of a mixt. of  $\bar{C}$  with isomeric 2,6-dichloro-3-hydroxybenzaldehyde (3:4160), m.p. 140°, is depressed to 111° (1)]

[For prepn. of  $\bar{C}$  from 4-chloro-3-hydroxybenzaldehyde (3:3780) in AcOH with  $Cl_2$  at room temp. (100% yield) see (1)]

$\bar{C}$  (1 pt.) in AcOH (4 pts.) on nitration at 65° with 1 pt. conc.  $HNO_3$  ( $D = 1.42$ ) yields (2) 2,4-dichloro-3-hydroxy-6-nitrobenzaldehyde (2), colorless ndls. from its deep yellow soln. in AcOH or from hot aq., m.p. 107° (2) (p-nitrophenylhydrazone, or. ndls. from AcOH, m.p. 279-280° (2), semicarbazone monohydrate, yel. ndls. from dil. alc., softens 140-150° (2))

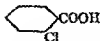
$\bar{C}$  dislvd. in boilg. 10% NaOH (2 moles) and treated with  $Me_2SO_4$  (1.3 moles) yields (1) 2,4-dichloro-3-methoxybenzaldehyde, m.p. 82° (1) (p-nitrophenylhydrazone, old-gold ndls., m.p. 258-260° (1)), which on oxidn. yields 2,4-dichloro-3-methoxybenzoic acid, colorless ndls., m.p. 163° (1)

⑤ 2,4-Dichloro-3-hydroxybenzaldehyde: fine colorless ndls. from alc., m.p. 188° (1).

⑥ 2,4-Dichloro-3-hydroxybenzaldehyde p-nitrophenylhydrazone: or.-red ndls., m.p. 277-278° dec (1)

3:4140 (1) Hodgson, Beard, *J. Chem. Soc.* 1926, 147-155. (2) Hodgson, Beard, *J. Chem. Soc.* 1926, 2030-2036.

### 3:4150 o-CHLOROBENZOIC ACID



$C_7H_5O_2Cl$  Beil. IX - 334  
IX<sub>1</sub>-(138)

M.P. 142°	(1) (2) (3)	139.9°	(15)
141.8°	(4)	139.8-140.0°	(16)
141°	(5) (6) (7) (8) (181)	139.5-140°	(17)
140-142°	(9)	139.5°	(38)
140.65°	(10)	139-140°	(18) (19)
140.3°	(11) (29)	130°	(20) (21) (22)
140.2°	(12)	138°	(23) (24) (58)
140°	(13) (14) (26) (27) (49)	137°	(25) (63) (97) (36)

Cryst. from hot aq.,  $C_6H_6$ , dioxane/ $C_6H_6$ , or alc. —  $\bar{C}$  is spar. sol. cold aq.; e.g.,  $\bar{C}$  is sol. at 0° in 881 pts. aq. (27); at 25°, 100 ml. satd. aq. soln. coats. 0.213 g  $\bar{C}$  (21) (= 0.0136 mole per liter (21) (28)). —  $\bar{C}$  is eas. sol. hot aq., alc., ether (26). — At 14–16°C 100 ml. satd. soln. of  $\bar{C}$  in acetone coats. 28.4 g  $\bar{C}$ , in ether 17 g  $\bar{C}$ , in EtOAc 13.2 g  $\bar{C}$ , in 75% AcOH 6.2 g  $\bar{C}$ ; in  $C_6H_6$  0.9 g  $\bar{C}$ ; in  $CCl_4$  0.6 g  $\bar{C}$ ; in  $CS_2$  0.5 g  $\bar{C}$ ; in 1 gr. 0.07 g  $\bar{C}$  (10). — For study of soly. of  $\bar{C}$  in acetone (4),  $C_6H_6$  (4) (29), heptane (29), chlorobenzene (3:7903) (30), o-chlorotoluene (3:8245) (30), or m-chlorotoluene (3:8275) (30) see indic. refs.

For study of distribution at 25° of  $\bar{C}$  between aq. + toluene (31), aq. + xylene (32), or aq. +  $CHCl_3$  (31) (32) (for use of  $CHCl_3$  in sepn. of  $\bar{C}$  from aq. suspension of 3-chlorophthalic acid (3:4820) (33)) see indic. refs.; for adsorption of  $\bar{C}$  on charcoal from its solns. in EtOH (34), acetone (4),  $C_6H_6$  (4), or aq. (35) see indic. refs.; for soly. of  $\bar{C}$  in aq. solns. of various salts (including  $Na\bar{A}$ ) see (28) (21).

$\bar{C}$  can be sublimed in vac. (12). —  $\bar{C}$  is but very slightly volatile with steam (for details see (11)). — For crystallographic data see (36) (37). — For purification of  $\bar{C}$  (by use of decolorizing carbon on soln. of  $\bar{C}$  in aq.  $Na_2CO_3$  followed by reprecipn. with 6 N HCl) see (33).

Binary systems contg.  $\bar{C}$ : for f.p./compn. data on system  $\bar{C}$  +  $H_2O$  see (39); for f.p./compn. data and diagram on system  $\bar{C}$  +  $BzOH$  (1:0715), eutectic, m.p. 91.1°, contg. about 41 wt. %  $\bar{C}$ , see (10) (41); for f.p./compn. data on systems  $\bar{C}$  + o-toluic acid (1:0690) (20) or  $\bar{C}$  + o-hydroxybenzoic acid (salicylic acid) (1:0780) (20) see indic. refs.

For f.p./compn. data and diagrams on systems  $\bar{C}$  + m-chlorobenzoic acid (3:4392) (eutectic, m.p. 110.7°, contg. 52–53 mole %  $\bar{C}$  (6) (40) (10) (15)) see indic. refs.; on system  $\bar{C}$  + p-chlorobenzoic acid (3:4940) (eutectic, m.p. 132°, contg. abt. 86 mole %  $\bar{C}$ ) see (10) (15).

For f.p./compn. data and diagrams on systems  $\bar{C}$  + o-bromobenzoic acid (41),  $\bar{C}$  + o-iodobenzoic acid (42),  $\bar{C}$  + o-nitrobenzoic acid (43),  $\bar{C}$  + m-nitrobenzoic acid (43) see indic. refs.

Ternary systems contg.  $\bar{C}$ . [For influence of addn. of benzoic acid (6) or of p-chlorobenzoic acid (3:4940) (40) to the eutectic of  $\bar{C}$  with m-chlorobenzoic acid (3:4392) see indic. refs.; for influence of addn. of  $\bar{C}$  to the eutectic of benzoic acid with m-chlorobenzoic acid see (40); for data on system  $\bar{C}$  + m-chlorobenzoic acid (3:4392) + p-chlorobenzoic acid (3:4940), eutectic, m.p. 104.9°, contg. respectively 48.3, 44.0, and 7.7 mole % of the three isomers, see (15).]

Miscellaneous. [For study of fate of  $\bar{C}$  in animal organism see (44) (45); note that contrary to earlier (45) results with dogs and rabbits conjugation with glycine to yield the expected N-(o-chlorobenzoyl)glycine (o-chlorobiphenyl acid) [Beil. IX-336], m.p. 176° (45), does (44) occur. — For study of use of  $\bar{C}$  (or its salts) as preservatives see (46); for detectn. of  $\bar{C}$  in foods see (179). — For use of  $\bar{C}$  as vulcanization regulator see (47) (48).]

Preparation. [For prepn. of  $\bar{C}$  from o-chlorotoluene (3:8245) by oxidn. with boilg. aq.  $KMnO_4$  (yields: 90% (14), 74–78% (18), 68–71% (24)) (49) (13), with nitrosulfonic acid (from fung.  $HNO_3$  + dry  $SO_2$ ) at 100° (50), with air in the pres. of various catalysts (51) (52) (53), or in aq. alk. at 260° under press. (54), see indic. refs.; for formn. of  $\bar{C}$  from o-chlorophenyl benzyl ketone by auto-oxidn. in light and air see (56); for formn. of  $\bar{C}$  from o-chlorobenzaldehyde (3:6410) by oxidn. with  $CrO_3$  (57), with alk.  $KMnO_4$  (58), or by auto-oxidn. in  $Ac_2O$  (59) see indic. refs.]

[For prepn. of  $\bar{C}$  from o-aminobenzoic acid (anthranilic acid) [Beil. XIV-312, XIV-1 (529)] via diazotization and use of  $Cu_2Cl_2$  (yields: 90% (24), 87% (178)) (preferably under  $CO_2$  (60)), or  $CuH$  (60% yield (61)), or  $Cu$  (62) see indic. refs.]

[For prepn. of  $\bar{C}$  from o-chlorobenzonitrile [Beil. IX-336] by hydrolysis with  $H_2SO_4$  (14), with dil. HCl in s.t. at 150° (63), or boilg. KOH (14) see indic. refs.; from o-chlorobenzoyl chloride (3:6640) by hydrolysis with aq. (91) or aq. alk.; from o-chlorobenzotri-

chloride (3:6880) by hydrolysis (64) (65), e.g., with aq. in s.t. at 150° (27) or by boilg. conc.  $\text{HNO}_3$  (65) see indic. refs.; from *o*-chlorobenzal (di)chloride (3:6625) with  $\text{CrO}_3$  (57) or with boilg. aq. for 20 hrs. followed by oxidn. with  $\text{KMnO}_4$  (75% yield (7)); from a mixt. of *o*-chlorobenzotrichloride + *o*-chlorobenzal (di)chloride by bydrol. with 70%  $\text{H}_2\text{SO}_4$  or 80%  $\text{AcOH}$  or 5%  $\text{NaOH}$  at 90–100° in stream of air to effect immediate oxidn. (67); from *o*-chlorobenzoyl-*o*-chlorotriphenylethane by hydrolytic cleavage with 20%  $\text{MeOH/KOH}$  5 hrs. at b.p. (8); from *o*-chlorophenylnitrolic acid by hydrolysis with boilg. aq. (19) see indic. refs.]

[For formn. of  $\bar{\text{C}}$  (together with other prods.) from benzoic acid (1:0715) with  $\text{KClO}_3$  +  $\text{HCl}$  (68), with  $\text{NaOCl}$  (6) (69), see indic. refs.]

[For formn. of  $\bar{\text{C}}$  from *o*-sulfobenzoic acid imide (saccharin) [Beil. XXVII-168, XXVII-1-(266)] with  $\text{KClO}_3$  +  $\text{HCl}$  see (9); from 3-chlorophthalic acid (3:4820) by cat. monodecarboxylation see (70); from *o*-nitrotoluene [Beil. V-318, V<sub>1</sub>-(158), V<sub>2</sub>-(243)] (71), from sodium *o*-toluenesulfonate [Beil. XI-83, XI<sub>1</sub>-(22)] (72), or from *o*-toluenesulfonyl chloride [Beil. XI-86, XI<sub>1</sub>-(23)] (71) with  $\text{SOCl}_2$  in s.t. at elevated temp. followed by treatment with aq. see indic. refs.]

Chemical behavior. [ $\bar{\text{C}}$  (as  $\text{Na}\bar{\text{A}}$ ) on reduction with  $\text{Na/Hg}$  (27) (25) (73) or  $\bar{\text{C}}$  (as  $\text{K}\bar{\text{A}}$ ) on fusion with sodium formate (74) cf. (75) is dehalogenated yielding benzoic acid (1:0715) (for study of reduction of  $\bar{\text{C}}$  with  $\text{H}_2$  +  $\text{Ni}$  in aq. alk. at ord. temp. see (76)). —  $\bar{\text{C}}$  on electrolytic reduction in alc.  $\text{H}_2\text{SO}_4$  yields (77) *o*-chlorobenzyl alc. [Beil. VI-444, VI<sub>1</sub>-(222)], ndls. from aq. alc., m.p. 72° (77)]

$\bar{\text{C}}$  behaves normally as a monobasic acid: e.g.,  $\bar{\text{C}}$  on titration with standard dil. aq. alk. gives Neut. Eq. 150.5; ionization const. at 25° is  $13.2 \times 10^{-4}$  (78) (79) cf. (80) (81) (21) (1). — [For study of acid strength of  $\bar{\text{C}}$  in various alcohols (82) (83) (84) (5) (85) (86) (22) or in acetonitrile (87) see indic. refs. — For solubility of  $\bar{\text{C}}$  in aq. solns. of various salts incl.  $\text{Na}\bar{\text{A}}$  see (28) (21). — For sepn. of  $\bar{\text{C}}$  from *p*-chlorobenzoic acid (3:4940) by use of difference in their acidic strength see (88) — For use of  $\bar{\text{C}}$  as standard in alkalimetry (89) and in iodimetry (90) see indic. refs.]

Salts of inorg. bases. [ $\text{NH}_4\bar{\text{A}}$  (91) (92) (note that this salt with benzotrichloride (3:6880) in pres. of suitable cat. yields (93) *o*-chlorobenzonitrile). — Hydroxylamine salt: m.p. 104.5° (94). —  $\text{Na}\bar{\text{A}}$  (use as preservative) (46). —  $\text{K}\bar{\text{A}} \cdot \frac{1}{2}\text{H}_2\text{O}$  (91) (forms liq. cryst. on fusion (95)). —  $\text{Ag}\bar{\text{A}}$ , scales from boilg. aq. (25) (100) (note that this salt with  $\text{I}_2$  in  $\text{C}_6\text{H}_6$  under reflux does not (96) yield phenyl *o*-chlorobenzoate, m.p. 37°, and thus differs from corresp. salt of *m*-chlorobenzoic acid (3:4392)) —  $\text{Ca}\bar{\text{A}}_2 \cdot \text{H}_2\text{O}$  (26) (97), much more sol. aq. than corresp. salts of *m*-chlorobenzoic acid (3:4392) or *p*-chlorobenzoic acid (3:4940) (97); insol. either cold or hot alc. (98); on dry distn. gives (18% yield (99)) xanthone (1:7275), m.p. 174° —  $\text{Ba}\bar{\text{A}}_2 \cdot 3\text{H}_2\text{O}$  from spont. evapn. of aq. soln. (98) (9). —  $\text{Ba}\bar{\text{A}}_2$  from hot conc. aq. soln. (25) (26) (use in sepn. of  $\bar{\text{C}}$  from isomers (40)); spar. sol. aq. (100). — Note that  $\text{Pb}\bar{\text{A}}_2$  (25) (100) and  $\text{Cu}\bar{\text{A}}_2$  (25) (100) are spar. sol. aq., while salts of  $\text{Ca}$ ,  $\text{Sr}$ ,  $\text{Mg}$ ,  $\text{Zn}$ ,  $\text{Fe}$ ,  $\text{Mn}$ ,  $\text{Co}$ ,  $\text{Ni}$ , and  $\text{Cd}$  are sol. (100). — For sepn. of  $\bar{\text{C}}$  from  $\text{BzOH}$  (1:0715) by use of  $\text{Cu}$  salts see (6)]

Salts of organic bases.  $\bar{\text{C}}$  with equiv. nmt. benzylamine in boilg.  $\text{EtOAc}$  followed by evapn. of solvent yields (101) benzylammonium *o*-chlorobenzoate, m.p. 148.4–149.4° u.c., 150.5–151.5° cor., Neut. Eq. 263.6 (note that the m.p. of this salt is but very slightly dif. from that of corresp. salt of *m*-chlorobenzoic acid (3:4392)). —  $\bar{\text{C}}$  similarly treated with  $\alpha$ -phenylethylamine yields (101)  $\alpha$ -phenylethylammonium *o*-chlorobenzoate, m.p. 128.4–129.4° u.c., 130.9–131.9° cor., Neut. Eq. 277.6 (note that m.p. of this salt, although better separated from those of the isomeric acids than the preceding case, is very close to those of the corresp. salts of *m*-methoxybenzoic acid, *p*-methoxybenzoic acid, and *o*-nitrobenzoic acid).



$\bar{C}$  (1 mole) in alc. mixed with codeine (1 mole), m.p. 155°, htd. several minutes, solvent evapd. and resulting sirup recrystd. from aq. yields (102) codeine *o*-chlorobenzoate,  $C_{15}H_{21}O_3N \cdot \bar{C}$ , m.p. 134° on "Maquenne block"; note that this value although close to that of corresp. prod. from *o*-bromobenzoic acid is widely different from that of corresp. salts of either *m*-chlorobenzoic acid (3:4392) or *p*-chlorobenzoic acid (3:4940) which are 96° and 162° respectively. —  $\bar{C}$  (1 mole) in alc. (or  $CHCl_3$ ) with strychnine (1 mole) in alc., boiled for a few minutes, then cooled, yields (103) strychnine *o*-chlorobenzoate,  $C_{21}H_{27}O_2N_2 \cdot \bar{C}$ , m.p. 170° u.c. on "Maquenne block"; note that this melting point is somewhat lower than that (185°) for the corresp. salt of *m*-chlorobenzoic acid (3:4392) and widely different from that (251°) of the corresp. salt of *p*-chlorobenzoic acid (3:4940).

[For optical data on cinchonine salt see (104); for salt (m.p. 108–110°) with phenylmercuric hydroxide see (105).]

$\bar{C}$  with alcohols gives by conventional processes the corresp. esters; for details on methyl *o*-chlorobenzoate (3:6695) and ethyl *o*-chlorobenzoate (3:6800) see these compds. — [For study of rate of esterification of  $\bar{C}$  with MeOH (106) (111) (17) (112), with EtOH (2) (17) (113), or with cyclohexanol (1:6415) (107) see indic. refs.]

$\bar{C}$  with  $P_2O_5$  in toluene boiled for 4 hrs. (108), or  $\bar{C}$  (109) or its sodium salt (110) refluxed with oxalyl (di)chloride (3:5060) in  $C_6H_6$ , yields *o*-chlorobenzoic acid anhydride, nlds. from lt. pet. (108) or nlc. (109), m.p. 79.6° (108), 78–79° (109); note that  $\bar{C}$  (2 moles) with oxalyl (di)bromide refluxed in  $C_6H_6$  similarly gives good yields (110) of the above anhydride, but that NaA with oxalyl (di)bromide can also be used (110) to give *o*-chlorobenzoyl bromide, h.p. 143–145° at 37 mm. (110).

$\bar{C}$  with  $PCl_5$  (114) (45) (115), or with  $PCl_5 + ZnCl_2$  (114), or with  $SOCl_2$  (114) (45) (116) (117), or with  $SOCl_2 +$  pyridine (118), or with *o*-chlorobenzotrichloride (3:6880) +  $ZnCl_2$  (119) yields *o*-chlorobenzoyl chloride (3:6640) q.v. for data on yields.

$\bar{C}$  with KOH or NaOH on fusion (128) (27) (25), or  $\bar{C}$  with aq. piperidine in pres. of Cu powder in s.t. at 160° for 4 hrs. (121), or  $\bar{C}$  with aq. piperidine +  $Na_2CO_3$  + amyl alc. + Cu powder refluxed 6 hrs. (124), or  $\bar{C}$  (as  $K\bar{A}$ ) with aq. NaOAc +  $Cu(OAc)_2$  in s.t. at 140–150° for 9–10 hrs. (126), or  $\bar{C}$  with aq.  $Ca(OH)_2$  + Cu cpds. at 160–170° under press. (122) gives (83% yield (126)) *o*-hydroxybenzoic acid (salicylic acid) (1:0780), accompanied in some cases (120) by substantial amounts of *m*-hydroxybenzoic acid (1:0825). — For use of alk. fusion as means of detect. of  $\bar{C}$  in wine see (123). — Note that  $\bar{C}$  with aq. KOH (even in pres. of copper) (124), or  $\bar{C}$  with aq.  $Ba(OH)_2$  in s.t. at 190–200° (125), does not yield salicylic acid or any chloride ion.

Reaction of  $\bar{C}$  with phenols.  $\bar{C}$  on suitable treatment condenses with phenols yielding *o*-aryloxybenzoic acids: e.g.,  $\bar{C}$  (as  $K\bar{A}$ ) with Na phenolate and Cu powder at 180–190° for 5 min. (127) (128), or  $\bar{C}$  (as  $K\bar{A}$ ) with phenol + Cu powder or Cu salts (129) (130), or  $\bar{C}$  (as  $K\bar{A}$ ) with anhydrous KOAc/NaOAc + Cu powder at 245–255° for 5 hrs. (126) gives (90% yield (127)) *o*-phenoxybenzoic acid [Beil. X-65,  $X_1$ -(28)], lfts. from dil. alc., m.p. 113°; note that this prod. with conc.  $H_2SO_4$  on gentle warming loses  $H_2O$  and ring-closes in quant. yield (131) to xanthone (1:7275), m.p. 174°. — [For analogous condensations of  $\bar{C}$  with *o*-cresol (1:1400) (127) (128) (60), *m*-cresol (1:1730) (127), *p*-cresol (1:1410) (127) (128),  $\alpha$ -naphthol (1:1500) (132),  $\beta$ -naphthol (1:1540) (127) (128), *o*-chlorophenol (3:5980) (133), *m*-chlorophenol (3:0255) (133), *p*-chlorophenol (3:0495) (133), *m*-nitrophenol (133), *p*-nitrophenol (133), including conv. to the corresp. xanthenes, see indic. refs.; many other analogous cases are known but cannot be included here.

Reaction of  $\bar{C}$  with amines.  $\bar{C}$  (or its salts) with primary or secondary aliphatic or aromatic amines in the pres. of  $K_2CO_3$  and Cu powder on htg. condenses with elimination of HCl (or its equivalent) to yield products of type *o*-HOOC- $C_6H_4$ -NHR; these products by ring closure through elimination of water yield in turn the corresponding acridones; the

reaction has been executed for countless cases of which only a few of the more important examples can be cited here; for the most comprehensive single survey see (134).

$\bar{C}$  (as  $K\bar{A}$ ) htd. with aq. aniline + Cu powder (134) (135), Cu salts (135), or  $\bar{C}$  htd. with aniline + Cu powder (136) or Cr powder (137), or  $\bar{C}$  htd. with aniline + anhydrous  $K_2CO_3$  + CuO (134) (38) gives (yields: 97% (134), 82-93% (38), 87% (137)) *N*-phenylanthranilic acid (diphenylamine- $\alpha$ -carboxylic acid) [Beil XIV-327, XIV<sub>1</sub>-(533)], cryst. from alc., m.p. 182-183° rap. htg (38); this prod. with conc.  $H_2SO_4$  at 100° loses aq. and ring-closes (yields 91-96% (33)) (138) (139) to acridone [Beil XXI-335, XXI<sub>1</sub>-(312)], sublimable yel. ndls., m.p. 354° cor.

[For details on analogous reaction of  $\bar{C}$  with  $\alpha$ -toluidine (134) (135) (136) (140), *m*-toluidine (134) (141), *p*-toluidine (134) (135),  $\alpha$ -naphthylamine (134) (135),  $\beta$ -naphthylamine (134) (135),  $\alpha$ -aminophenol (134),  $\alpha$ -anisidine (134), *m*-anisidine (134) (141), *p*-anisidine (142),  $\alpha$ -aminobenzoic acid (134), *m*-aminobenzoic acid (134), *p*-aminobenzoic acid (134), *p*-phenylenediamine (134), *p*-aminodimethylaniline (124), see indie. refs.; scores of other examples cannot be cited here.]

Substitution of nucleus of  $\bar{C}$ . — [ $\bar{C}$  in fuming  $H_2SO_4$  or chlorosulfonic acid + a little sulfur treated with  $Br_2$  (1 mole) at 60-70° gives (70-75% yield (143)) 5-bromo-2-chlorobenzoic acid [Beil IX-355], ndls., m.p. 165-167° (143).]

$\bar{C}$  on mononitration under various conditions, e.g.,  $\bar{C}$  (2 wt. pts) dislvd. in conc.  $H_2SO_4$  (15 wt. pts) and treated below 50° with a mixt. of  $HNO_3$  ( $D = 1.5$ ) (1 wt. pt.) in conc.  $H_2SO_4$  (2.5 wt. pts) (144) gives mainly (yields: 78.5% (144), 85% (145), 32-38% (146)) (147) (148) (14) (149) 2-chloro-5-nitrobenzoic acid [Beil IX-403], ndls. from aq., m.p. 165° (149) (14) (172), 164-165° (144) (145), 164° (146) (148), accompanied by a small amt. 2-chloro-3-nitrobenzoic acid [Beil IX-402], m.p. 185° (148), 181° (150). — [Note that both the other nitro-2-chlorobenzoic acids are known, viz., 2-chloro-4-nitrobenzoic acid [Beil IX-404], ndls. from aq., m.p. 140° (151), 139-140° (152), and 2-chloro-6-nitrobenzoic acid, m.p. 161° (151), but are prepd. by other methods.]

$\bar{C}$  on direct dinitration, e.g., with conc.  $H_2SO_4$  +  $KNO_3$  at 100° (153) (154) or at 130° (155) or  $\bar{C}$  with conc.  $H_2SO_4$  + fuming  $HNO_3$  at 130-140° (156), gives (94% yield (155)) 2-chloro-3,5-dinitrobenzoic acid [Beil IX-415], ndls. from aq., m.p. 199-200° (153) (154), 199° (156), 193.5° cor. (155) (for use of this prod. in detection of  $\bar{C}$  see (180)); this prod. is also obtd. by further nitration of 2-chloro-3-nitrobenzoic acid (above) with conc.  $H_2SO_4$  +  $KNO_3$  at 170° (157). — [Note that of the 5 other isomeric dinitro-2-chlorobenzoic acids which are possible only one is known, viz., 2-chloro-4,5-dinitrobenzoic acid, m.p. 165° cor. (158), obtd. from 2-chloro-4-nitrobenzoic acid (above) by further nitration with fuming  $HNO_3$  + conc.  $H_2SO_4$  (80% yield (158)).]

— Methyl *o*-chlorobenzoate: oil, b.p. 234°. (See 3:6695.)

— Ethyl *o*-chlorobenzoate: oil, b.p. 243°. (See 3:6800.)

① *p*-Nitrobenzyl *o*-chlorobenzoate: m.p. 106° (159). [From  $\bar{C}$  (as  $Na\bar{A}$ ) with *p*-nitrobenzyl bromide (m.p. 99°) in boilg. dil. alc. (159); note that the m.p. of this ester is almost identical with that (107°) of the corresp. prod. from *m*-chlorobenzoic acid (3:4392).]

② Phenacyl *o*-chlorobenzoate: m.p. 85.5° (160), 83° (23). [From  $\bar{C}$  (as  $Na\bar{A}$ ) with phenacyl bromide (m.p. 50°) in boilg. alc. (97% yield (23)).] — [Note that the m.p. of this prod. is only slightly lower than that (87.6°) of the corresp. prod. similarly obtd. from *p*-chlorobenzoic acid (3:4940).]

— *p*-Chlorophenacyl *o*-chlorobenzoate: unreported.

③ *p*-Bromophenacyl *o*-chlorobenzoate: m.p. 107.0° cor. (161), 106° (23) (162). [From  $\bar{C}$  (as  $Na\bar{A}$ ) with *p*-bromophenacyl bromide (m.p. 109°) in boilg. alc. (80% yield (23)).]

— *p*-Iodobenzenyl *o*-chlorobenzoate: unreported.

① *p*-Phenylphenacyl *o*-chlorobenzoate: m.p. 123° (163). [From  $\bar{O}$  (as Na $\bar{A}$ ) with *p*-phenylphenacyl bromide (m.p. 126°) in boilg. alc. (163).]

— *S*-Benzylthiuronium *o*-chlorobenzoate: unreported.

② *S*-(*p*-Chlorobenzyl)thiuronium *o*-chlorobenzoate: cryst. from dioxane, m.p. 159° cor. (164). [From  $\bar{C}$  (as Na $\bar{A}$  or K $\bar{A}$ ) in nq. with 1 equiv. of *S*-(*p*-chlorobenzyl)-thiuronium chloride, m.p. 197° (10% in nlc.) (164); note that the m.p. of this prod. is closely adjacent to that (m.p. 157° cor.) of the corresp. salt of *m*-chlorobenzoic acid (3:4392).]

③ *S*-(*p*-Bromobenzyl)thiuronium *o*-chlorobenzoate: m.p. 168° cor. (165). [From  $\bar{C}$  (as K $\bar{A}$  or Na $\bar{A}$ ) in nq. with 1 equiv. of *S*-(*p*-bromobenzyl)thiuronium bromide (m.p. 213°) in nlc. (165); note that m.p. of this prod. is only slightly higher than that (163° cor.) for the corresp. prod. from *p*-chlorobenzoic acid (3:4940).]

④ *o*-Chlorobenzamide: cryst. from alc. or alc./ether, m.p. 142.4° cor. (166), 142° (167), 141° (14), 140.5° (91), 139° (25). [From  $\bar{C}$  by refluxing with AcOH + (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (37–39% yield (167)), from *o*-chlorobenzoyl chloride (3:6640) with conc. aq. NH<sub>4</sub>OH (166) (14) (01) (25), or from ethyl *o*-chlorobenzoate (3:6800) with conc. aq. NH<sub>4</sub>OH (25).] — [Note that *o*-chlorobenzamido on htg. with AlCl<sub>3</sub>.NaCl (large excess) gives (93% yield (168)) *o*-chlorobenzonitrile [Beil. IX-330], m.p. 43–44° (168), 42–43° (169), b.p. 232° (169).]

⑤ *o*-Chlorobenzhydrazide: ndls. from alc., m.p. 117–118° (170), 109–110° (171). [From ethyl *o*-chlorobenzoate (3:6800) q.v. with hydrazine hydrate (170) (171); for use as reagt. for identification of aldehydes and ketones see (170).]

— *N*-(*o*-Chlorobenzoyl) *N*-phenylhydrazide: unreported.

⑥ *o*-Chlorobenzanilide: ndls. from alc. or pet. ether; m.p. 114° (172) (173) (174), 117–118° (175) (176). — [From *o*-chlorobenzoyl chloride (3:6640) with excess aniline (25) (172) in pres. of a tertiary amine (80% yield (174)); also from oxime of *o*-chlorobenzophenone (3:0715) by Beckmann rearr. (175) (173) (176).] — [Note that this prod. must not be confused with benz-*o*-chloroanilide, m.p. 99–100°.]

⑦ *o*-Chlorobenz-*p*-toluidide: cryst. from dil. alc., m.p. 131° (177). [From *o*-chlorobenzoyl chloride (3:6640) with *p*-toluidine (177).]

— *o*-Chlorobenz- $\alpha$ -naphthalide: unreported.

— *o*-Chlorobenz- $\beta$ -naphthalide: unreported.

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3:4155 5,8-DICHLORONAPHTHOL-2



$C_{10}H_6OCl_2$

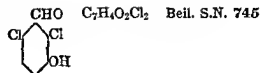
Beil. S.N. 538

M.P. 141-142° (1)

[For prepn. from 5,8-dichloro-2-aminonaphthalene by hgt. with dil.  $H_2SO_4$  for 8 hrs. at 195-205° under pressure see (1) (2).]

— 5,8-Dichloro-2-naphthyl methyl ether: m.p. 74° (2).

3:4155 (1) Soc. Chem. Ind., Basel, Swiss 202,854, May 1, 1939; *Cent.* 1939, II 3196. (2) Goldstein, Viaud, *Helv. Chim. Acta*, 27, 883-888 (1944); C.A. 39, 926 (1945).

**3:4160 2,6-DICHLORO-3-HYDROXYBENZ-  
ALDEHYDE**


M.P. 142-142.2° (1)  
140.5° cor. (2) (3)  
140° (4)

Colorless cryst. from hot aq —  $\bar{C}$  has pronounced sternutatory properties and also attacks moist skin producing painful blisters. — [ $\bar{C}$  when mixed with 2-chloro-3-hydroxybenzaldehyde (3:4085), m.p. 139.5° (4), depresses m.p. to 116° (4)]

[For prepn. of  $\bar{C}$  from *m*-hydroxybenzaldehyde (1:0055) with  $Cl_2$  (2 moles) in AcOH soln. (yields: 51.5% (2) cf (3), 38% (4)) (1) (other prods. also being formed) see indic. refs; from 2-chloro-3-hydroxybenzaldehyde (3:4085) with  $Cl_2$  (1 mole) in AcOH see (4); from 6-chloro-3-hydroxybenzaldehyde (3:3350) with  $Cl_2$  (1 mole) in AcOH ( $\bar{C}$  is main prod (5) but 4,6-dichloro-3-hydroxybenzaldehyde (3:3952) is also formed (4) (5)) see indic. refs]

[For condens. of  $\bar{C}$  with *p*-chlorophenol (3:0475) and use of prod. as mothproofing agent see (6); for condens. of  $\bar{C}$  with 2,4-dihydroxybenzoic acid (1:0843) (7) or with *o*-cresotinic acid (2-hydroxy-3-methylbenzoic acid) (8) and use of products as dye intermediates see indic. refs]

$\bar{C}$  in 50% aq KOH at 60-70° first ppts. yel. K salt of  $\bar{C}$  which grad. dissolves and is replaced by a colorless cryst. ppt.; after atdg. 4 hrs. acidification with dil.  $H_2SO_4$  gives (93.8% yield (2)) 2,4-dichlorophenol (3:0560), m.p. 42° (2).

$\bar{C}$  in AcOH with  $Br_2$  gives (70% yield (3)) 4-bromo-2,6-dichloro-3-hydroxybenzaldehyde, cryst. from  $C_6H_6$  + lgr, m.p. 104-105° (3) (methyl ether, m.p. 82°, oxime, m.p. 193° cor. (3)).

$\bar{C}$  (1 pt.) in AcOH (4 pts) on nitration with 1 pt. conc.  $HNO_3$  ( $D = 1.42$ ) at 65° yields (4) 2,6-dichloro-3-hydroxy-4-nitrobenzaldehyde, bright yel. ndls. from AcOH or pl. from aq, m.p. 80° (4) (Ag salt, crimson ndls. from hot aq; oxime, deep yel. ndls. from dil. alc., m.p. 195°; *p*-nitrophenylhydrazone, deep red ndls. from hot AcOH, m.p. 279-280° dec.; semicarbazone, light-yel. lfts. from hot alc, m.p. 255-256° (4)).

$\bar{C}$  dislvd. in hot aq.  $NaHCO_3$  and treated with  $Me_2SO_4$  for 15 min. yields (4) (3) the corresp. methyl ether, viz., 2,6-dichloro-3-methoxybenzaldehyde, m.p. 103-104° (3), 102° (4) (*p*-nitrophenylhydrazone, old-gold ndls., m.p. 214-215° (4)); this methyl ether upon oxidn. with alk.  $KMnO_4$  gives (4) 2,6-dichloro-3-methoxybenzoic acid, ndls. from dil. alc, m.p. 149.5° (4).

① 2,6-Dichloro-3-hydroxybenzaldehyde oxime: ndls. from dil. alc., m.p. 174-175° (4).

② 2,6-Dichloro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazone: deep or.-red. ndls., m.p. 205-206° (4).

**3:4160** (1) Bissell, Kranz (to National Aniline and Chem. Co.) U.S. 1,778,802, Sept. 20, 1929; *Cent.* 1931, I 159; *C.A.* 24, 5768-5769 (1930). (2) I *Monatsh.* 62, 184-185, 193-194 (1933). (4) Hodgson 152-153, 155 (5) Hodgson, Beard, *J. Chem. Soc.* 15 Stötter (to I.G.), *Ger.* 530,219, July 24, 1931; *Cent.* (to I.G.), U.S. 1,532,790, April 7, 1925; *Cent.* 1925, II 352. (8) I.G., Brit. 263,879, March 2, 1927; *Cent.* 1927, I 2364.

## 3:4170 3-CHLORONAPHTHOL-1

 $C_{10}H_7OCl$ 

Beil. VI —

VI<sub>1</sub>—VI<sub>2</sub>-(581)

M.P. 143° (1)

134-135° (2)

Nds. from lgr. (2),  $C_6H_6$ , alc. or 80% AcOH (1). — Volatile with steam (1).

[For prepn. of  $\bar{C}$  from 3-chloronaphthylamine-1 (1) via diazotization and of the diazonium salt with steam see (1); from 2,3,4-trichloronaphthol-1 [Beil. VI-613, by partial reduction with HI ( $D = 1.7$ ) in AcOH on boilg. 7 hrs. (100% yield) see (2).]

 $\bar{C}$  is sol. in aq. alk., and the result. soln. couples with solns. of diazonium salts (1).

$\bar{C}$  with  $Br_2$  aq. (and alk.?) gives 3-chloro-2,4-dibromonaphthol-1, pr. from 90% formic acid, m.p. 112° (1).

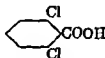
[ $\bar{C}$  in 10% aq. KOH shaken with  $Me_2SO_4$  for 20 min. gives (81% yield (2)) 3-chloronaphthol-1 methyl ether, oil, b.p. 162-164° at 18 mm. (2).]

① 3-Chloro-1-naphthyl acetate: nds. from lgr., m.p. 69° (2). [From  $\bar{C}$  with acetyl chloride in  $C_6H_6$  on refluxing 3 hrs. in  $C_6H_6$  (66% yield (2)).]

② 3-Chloro-1-naphthyl benzoate: nds. from lgr., m.p. 118-110° (2). [From  $\bar{C}$  in 10% aq. KOH on shaking with  $BzCl$  (71% yield (2)).]

3:4170 (1) Hodgson, Elliott, *J. Chem. Soc.* 1934, 1707. (2) Franzen, Stäuble, *J. prakt. Chem.* (2) 103, 385-387 (1922).

## 3:4200 2,6-DICHLOROBENZOIC ACID

 $C_6H_4O_2Cl_2$ 

Beil. IX - 343

IX<sub>1</sub>-(141)

M.P. 144° (1) (2)

143.7° (3)

143-144° (4)

141.5-142.5° (5)

Many recorded m.p.'s lower than these values [cf. ...] now known to have been impure.

Cryst. from lgr. (1) or mixt. of  $C_6H_6$  + lgr. (4, from alc. — Can also be purified by distn. in vac

[For prepn. of  $\bar{C}$  from 2,6-dichlorotoluene (3 to 2,6-dichlorobenzyl bromide, conversion to  $KMnO_4$  see (1) (4); from 2,6-dichloroben. ... older less satisfactory methods see Beil. IX-343.]

$\bar{C}$  on htg. begins to lose  $CO_2$  at 235° (5). [ $\bar{C}$  at 150° for 24 hrs. was recovered unchanged to ...]

$\bar{C}$  on nitration under stated conditions (1) gives acid, cryst. from toluene, m.p. 152° (1).

$\bar{C}$  (as  $K\bar{A}$ ) htd. with aniline +  $K_2CO_3$  + Cu in aminocarboxylic acid-2, cryst. from  $C_6H_6$ , m.p. 18 atoms.]

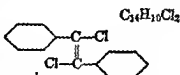
$\bar{C}$  htd. with acetamide for 6 hrs. at 225-235° (3:5960), b.p. 172°.

$\bar{C}$  htd. with  $PCl_5$  (6) or with  $SOCl_2$  + pyridine (4) b.p. 142-143° at 21 mm. (6). 126-128° at 18 mm. (7).

- Methyl 2,6-dichlorobenzoate: from  $\text{Ag}\bar{\text{A}} + \text{MeI}$  (8); b.p.  $250^\circ$  (8).  
 — Ethyl 2,6-dichlorobenzoate: from  $\text{Ag}\bar{\text{A}} + \text{EtI}$  (8) or from  $\bar{\text{C}}$  via  $\text{SOCl}_2$ , followed by  $\text{EtOH}$  (82% yield (5)); cannot be prepared by direct esterification (8); b.p.  $264-265^\circ$  (8). [This ester on htg. with  $\text{AlCl}_3$  at  $120-130^\circ$  for  $2\frac{1}{2}$  hrs. gives  $\text{EtCl}$  (91%) and  $\bar{\text{C}}$  (92%) (5).]  
 Ⓐ 2,6-Dichlorobenzamide: ndls. from alc., m.p.  $202^\circ$  (8),  $198^\circ$  (7). [This amide htd. with  $\text{NaCl}\cdot\text{AlCl}_3$  over free flame evolves  $\text{HCl}$  and gives (67% yield (5)) 2,6-dichlorobenzonitrile, ndls. from lgr., m.p.  $142.5-143.5^\circ$  (5),  $143^\circ$  (9); the nitrile can be reconverted to the amide with alk.  $\text{H}_2\text{O}_2$  (9).]  
 — 2,6-Dichlorobenzanilide: unrecorded.

3:4200 (1) Lehmstedt, Schrader, *Ber.* 70, 1530-1531 (1937). (2) Davies, *J. Chem. Soc.* 119, 873 (1927). (3) Morris, Bearse, *J. Am. Chem. Soc.* 62, 1432-1435 (1940). (4) Mint, Heinen, *J. prakt. Chem.* 71, 119 (1910). (5) Ref. 8, pp. 222-223. (10) Lock, Böck, *Ber.* 70, 922 (1937).

3:4210 *trans*-1,2-DICHLORO-1,2-DIPHENYLETHYLENE  
 (*trans*- $\alpha,\alpha'$ -Dichlorostilbene;  
*trans*-tolane dichloride)



Beil V ~ 634  
 $\text{V}_1$ -(304)  
 $\text{V}_2$ —

M.P. $153^\circ$	(1)	B.P. $316.5^\circ$ cor. at 767 mm. (20)
$150^\circ$	(2)	$183^\circ$ at 18 mm. (6)
$148^\circ$	(3)	
$143-144^\circ$	(4)	
$143^\circ$	(5) (6) (7) (13)	
$142.5^\circ$	(8)	
$142-143^\circ$	(17)	
$140-142^\circ$	(9)	
$141^\circ$	(19)	
$139-140^\circ$	(13)	
$139.5^\circ$	(10)	
$138-139^\circ$	(11)	

(4)  
 Ⓢ (See also *cis*-1,2-dichloro-1,2-diphenylethylene (3:1380).)  
 alc.]

Ⓢ Colorless tbs. from alc;  $\bar{\text{C}}$  is much less sol. in alc. than its *cis* isomer (3:1380); 100 pts.  $\bar{\text{C}}$  alc. at  $24.4^\circ$  dis. 0.71 pt.  $\bar{\text{C}}$ , but soly. of  $\bar{\text{C}}$  is diminished by pres. of its stereoisomer (10). —  $\bar{\text{C}}$  (like its isomer) is very sol. ether.

Note that  $\bar{\text{C}}$  (the higher-melting tolane dichloride) has now been shown (4) to have the *trans* configuration, many earlier reports to the contrary notwithstanding.

Note also that  $\bar{\text{C}}$  with 1,1,2,2-tetrachloro-1,2-diphenylethane (tolane tetrachloride) (3:4496) gives an isomorphous mixt. (2), formerly erroneously regarded as an individual cpd. designated as "ditolane hexachloride."

### PREPARATION OF $\bar{\text{C}}$

Note that in all processes (below) for prepn. of  $\bar{\text{C}}$  more or less of the lower-melting (*cis*) stereoisomer is always formed.



## FROM DINUCLEAR INITIAL MATERIALS

From diphenylacetylene (tolane). [For prepn. of  $\bar{C}$  from tolane [Beil. V-656, V<sub>1</sub>-(319), V<sub>2</sub>-(568)] with Cl<sub>2</sub> in CHCl<sub>3</sub> see (7).]

From trans-1,2-diphenylethylene (stilbene). [For prepn. of  $\bar{C}$  from stilbene (1:7250) with PCl<sub>5</sub> (2 moles) in POCl<sub>3</sub> at 170° see (12).]

From 1,1,2,2-tetrachloro-1,2-diphenylethane (tolane tetrachloride). [For prepn. of  $\bar{C}$  from tolane tetrachloride (3:4496) by removal of two adjacent chlorine atoms by use of Zn dust in EtOH (1) (6) (7) (10), Zn dust in AmOH (6), Fe powder in boilg. AcOH (14) (6) (note that in this method ratio of  $\bar{C}$  to lower m.p. stereomer is 1:5 (6)), or by use of excess conc. (2 N) MeMgCl (11), or with H<sub>2</sub> + hydrazine hydrate in MeOH/KOH at b.p. for 1½ hrs. (3) see indic. refs.]

From benzoin. [For formn. of  $\bar{C}$  from benzoin (1:5210) with PCl<sub>5</sub> at 0° (much benzoyl-phenyl-dichloromethane ("chlorohenzil") [Beil. VII-436, VII<sub>1</sub>-(234)] also being formed) see (20).]

## FROM MONONUCLEAR INITIAL MATERIALS

From henzotrichloride. [For prepn. of  $\bar{C}$  from henzotrichloride (3:6540) with Cu powder (yield of total mixed stereoisomers 68% (15), 23 5% (16) (17)), by action of excess conc. (2 N) MeMgCl (yield total mixed stereoisomers 22% (11)), by action of hydrazine hydrate + Pd in MeOH/KOH (35% yield (3)), or for formn. of  $\bar{C}$  (together with other products) by pyrolysis over hot Pt (18) see indic. refs.]

From benzal (di)chloride. [For formn. of  $\bar{C}$  (together with other prods.) from benzal (di)chloride (3:6327) by pyrolysis over hot Pt see (18).]

## FROM MISCELLANEOUS SOURCES

[For formn. of  $\bar{C}$  from CnC<sub>2</sub> with satd. soln. of Cl<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> see (13); from benzoyl-pbenyl-diazomethane (azibenzil) [Beil. VII<sub>1</sub>-(395), XXIV-208] with oxalyl (di)chloride (3:5060) in C<sub>6</sub>H<sub>6</sub> (38.5% yield  $\bar{C}$ ) see (9); from 1,1,2-trichloro-1,2-diphenylethanes [Beil. V-601] by elimination of HCl with alc. KOH see (19); for formn. of  $\bar{C}$  from its lower-melting stereoisomer (3:1380) by distn. (about 32% conversion to  $\bar{C}$  (10)) (12) (6) see indic. refs.]

CHEMICAL BEHAVIOR OF  $\bar{C}$ 

$\bar{C}$  on htg is partially transformed (6) (12) to the lower-melting isomer (3:1380); on distn. conversion is about 68% (10).

Reduction of  $\bar{C}$ .  $\bar{C}$  with conc. H<sub>2</sub> and red P in s.t. at 170° for 20 hrs. gives (16) (20) bibenzyl (1:7149), m.p. 52°.

Elimination of 2 chlorine atoms.  $\bar{C}$  with Na/Hg in alc. (1) (16), or  $\bar{C}$  with Zn dust in boilg. alc. (7) (10), or  $\bar{C}$  with alc. KOH in s.t. at 180° (12) gives diphenylacetylene (tolane) [Beil. V-656, V<sub>1</sub>-(319), V<sub>2</sub>-(568)], m.p. 60°.

Addn. of halogens.  $\bar{C}$  with Cl<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> soln. yields (13) 1,1,2,2-tetrachloro-1,2-diphenylethane (tolane tetrachloride) (3:4496). —  $\bar{C}$  does not (12) add Br<sub>2</sub>, and the expected prod. 1,2-dibromo-1,2-dichloro-1,2-diphenylethane is unreported from any other source.

Nitration of  $\bar{C}$ . The nitration of  $\bar{C}$  has never been studied, and neither mono nor dinitro derivs. are reported from any other source.

3:4210 (1) Zinin, *Ber.* 4, 288-289 (1871). (2) Marckwald, Karczag, *Ber.* 40, 2994-2995 (1907).  
 (3) Busch, Weber, *J. prakt. Chem.* (2) 146, 50-52 (1892). (4) Busch, Weber, *J. Chem. Soc.* 1936,  
 405. (5) Arends, *Ber.* 64, 1939 (1931). (6) (7)  
 ann, Homeyer, *Ber.* 12, 1973-1974 (1874). (8)  
 Staudinger, *Ber.* 49, 1971-1972 (1916). (10) :

... Chem. Soc. 55, 723 (1933). (12) Limpricht, *Schwanert, Ber.* 4, 379 (1918). (14) Lachowicz, *Ber.* 17, 1165 (2) 83, 115-116 (1911). (16) Hanhart, (1884). (18) Loeb, *Ber.* 36, 3060-3061 897. (20) Redsko, *J. Russ. Phys-Chem.*

3:4220 2,3-DICHLOROHYDROQUINONE  
(2,3-Dichloroquinol;  
o-dichlorohydroquinone)



$C_6H_4O_2Cl_2$  Bell. VI - 849  
VI<sub>1</sub>—  
VI<sub>2</sub>-(845)

M.P. 144-145° (1)  
144° (2) (3) (5)  
143° (4)

[See also 2,3-dichlorobenzoquinone-1,4 (3:2385).]

Ndls. from aq. with 2 H<sub>2</sub>O lost at 100° or over conc. H<sub>2</sub>SO<sub>4</sub> (1); eas. sol. alc., insol. cold lgr; sublimes.

(For prepn. of  $\bar{C}$  from hydroquinone (1:1590) in ether with SO<sub>2</sub>Cl<sub>2</sub> (1) (6), in AcOH with Cl<sub>2</sub> (30% yield (4)) (7) (6), in ether with EtOCl (3), or in MeOH with Cl<sub>2</sub> (9) see indie. refs.; from chlorobenzoquinone (3:1100) in ether with HCl gas (12% yield (5))

resultant diacetate (2)]

[For use as antioxidant and gum inhibitor in cracked gasoline see (10); in aq. petroleum emulsion as insecticidal oil spray see (11)]

$\bar{C}$  with FeCl<sub>3</sub> gives a greenish black quinhydrone (1).

$\bar{C}$  in AcOH with excess Br<sub>2</sub> yields (6) 4,5-dibromo-2,3-dichlorohydroquinone, golden-yellow lts from lgr, m.p. 294° (6).

$\bar{C}$  reduces NH<sub>4</sub>OH/AgNO<sub>3</sub> and Fehling's soln. (1);  $\bar{C}$  on oxidn. with MnO<sub>2</sub> + dil. H<sub>2</sub>SO<sub>4</sub> (1) (4) (5) or with CrO<sub>2</sub>/AcOH (7) gives (yields: 88% (4), 60% (1)) 2,3-dichlorobenzoquinone (3:2885) q.v. [For study of oxidn.-reductn. potential of  $\bar{C}$  see (4)]

② 2,3-Dichlorohydroquinone diacetate: colorless ndls. from dil. alc., m.p. 121° (6) (2). [From  $\bar{C}$  + Ac<sub>2</sub>O (6), or from p-benzoquinone dichloride (see above) with Ac<sub>2</sub>O + H<sub>2</sub>SO<sub>4</sub>, (2)]

③ 2,3-Dichlorohydroquinone dibenzoate: colorless cryst. from CS<sub>2</sub> or pet. ether, m.p. 173-174° (1). [From  $\bar{C}$  in dil. aq. alk. with BrCl (1).]

④ 2,3-Dichlorohydroquinone dimethyl ether: pinkish white ndls. from dil. alc., m.p. 124° (6). [From  $\bar{C}$  in dil. alk. with Me<sub>2</sub>SO<sub>4</sub> (6)] [Note that corresp. deriv. of 2,5-dichlorohydroquinone (3:4690) has m.p. 125-127° but that a mixt. of the two derivs. is depressed to m.p. 97° (6)]

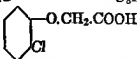
... Chem. Soc. 55, 723 (1933). (12) Limpricht, *Schwanert, Ber.* 4, 379 (1918). (14) Lachowicz, *Ber.* 17, 1165 (2) 83, 115-116 (1911). (16) Hanhart, (1884). (18) Loeb, *Ber.* 36, 3060-3061 897. (20) Redsko, *J. Russ. Phys-Chem.*

{11} Yates (to Shell Development Co.), U.S. 1,778,240, Oct. 14, 1930; *Cent.* 1931, 1 2799; C.A. 24, 5928 (1930).

**3:4260 o-CHLOROPHENOXYACETIC ACID**

 $C_8H_7O_3Cl$ 

Beil. VI —

VI<sub>1</sub>—VI<sub>2</sub>-(172)

M.P. 147.2-147.7° cor. {4}

145-146°

{1} {2} {3}

Neut. Eq. 186.5

Wh. ndls. (from hot nq.). [For prepn. from o-chlorophenol (3:5980) by hgt. with chloroacetic ac. (3:1370) and nq. nlk. see {1} {2} {3}.]

$\bar{C}$  refluxed with  $1\frac{1}{2}$  pts. thionyl chloride for  $1\frac{1}{2}$  hrs. gives (90% yield {1}) o-chlorophenoxyacetyl chloride, h.p. 136° at 12 mm., m.p. 18.4° {1}.

The methyl ester (b.p. 186-188°) and the ethyl ester, ndls. (from alc.), m.p. 32°, have been prepd. from the acid chloride {1} {5}

o-Chlorophenoxyacetamide: from the acid chloride by treatment with excess  $(NH_4)_2CO_3$ ; ndls. readily sol. in hot nq., alc., or  $C_6H_6$ , m.p. 149.5° {1}.

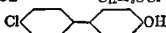
o-Chlorophenoxyacetanilide: from the acid chloride by action of aniline (2 moles) in  $C_6H_6$ ; ndls. (from alc.), m.p. 121° {1}.

**3:4260** {1} Minton, Stephen, *J. Chem. Soc.* 121, 1599-1601 (1922). {2} Behaghel, *J. prakt. Chem.* 114, 297-298 (1926). {3} Koelsch, *J. Am. Chem. Soc.* 53, 304-305 (1931). {4} Hayes, Branch, *J. Am. Chem. Soc.* 65, 1555-1564 (1943). {5} Bacher, Raiford, *Proc. Iowa Acad. Sci.* 50, 247-251 (1943), C.A. 38, 2327 (1944).

**3:4262 4-(p-CHLOROPHENYL)PHENOL**  
(4'-Chloro-4-hydroxybiphenyl)

 $C_{12}H_9OCl$ 

Beil. VI —

VI<sub>1</sub>—VI<sub>2</sub>-(635)

M.P. 146-147° {1}

145.5-146° {3}

145-146° {2}

[ $\bar{C}$  is best prepd. (nearly quant. yield {2}) by alk. hydrolysis of its acetate (see below) or by similar treatment (67% yield {3}) of its benzoate (see below) or (39% yield {3}) of its benzenesulfonate (see below); for formn. of  $\bar{C}$  from 4-amino-4'-hydroxybiphenyl by diazotization, etc., see {1}; from 4'-chloro-4-aminobiphenyl {2} by diazotization and hydrolysis see {2}.]

$\bar{C}$  on chlorination with  $Cl_2$  in  $CCl_4$  soln. gives (92% yield {4}) 2-chloro-4-(p-chlorophenyl)phenol, m.p. 71-72° (corresp. acetate, m.p. 74.5-75°; corresp. benzoate, m.p. 125-126°; corresp. benzenesulfonate, m.p. 100-101°) {4}.

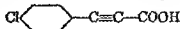
④ 4-(p-Chlorophenyl)phenyl acetate: m.p. 113° {2} [From  $\bar{C}$  by acetylation, or from the acetate of 4-hydroxybiphenyl (1:1585) with  $Cl_2$  in  $CCl_4$  + trace of  $I_2$  (47% yield {2}) or similarly in AcOH {5}.] [Note that the m.p. of this prod. has also been given without details of prepn. as 72° {6}.]

④ 4-(p-Chlorophenyl)phenyl benzoate: m.p. 182° {3}. [From  $\bar{C}$  by benzylation or from the benzoate of 4-hydroxybiphenyl (1:1585) with  $Cl_2$  in  $CCl_4$  soln. + trace of  $I_2$  (55% yield {3}).]

④ 4-(p-Chlorophenyl)phenyl benzenesulfonate: m.p. 74-75° {3}. [From  $\bar{C}$  with benzenesulfonyl chloride + aq. 10% NaOH {3}, or from the benzenesulfonate ester of 4-hydroxybiphenyl (1:1585) with  $Cl_2$  in  $CCl_4$  soln. + trace  $I_2$  (21% yield {3}).]

3:4262 (1) Angeletti, Gatti, *Gazz. chim. ital.* **53**, 633 (1928). (2) Savoy, Abernathy, *J. Am. Chem. Soc.* **64**, 2219-2221 (1942). (3) Savoy, Abernathy, *J. Am. Chem. Soc.* **64**, 2719-2720 (1942). (4) Savoy, Abernathy, *J. Am. Chem. Soc.* **65**, 1464-1465 (1943). (5) Schmidt, Savoy, Abernathy, *J. Am. Chem. Soc.* **65**, 296-297 (1943). (6) Hodgson, *J. Chem. Soc.* **1942**, 583.

3:4265 *p*-CHLOROPHENYLPROPIOLIC ACID  $C_9H_7O_2Cl$  Beil. S.N. 950



M.P. 147° (1)

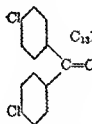
Cryst. from AcOH.

[For prepn. of  $\bar{C}$  from *p*-chlorobenzaldehyde (3:0765) by conversion through *p*-chlorocinnamic acid to ethyl *p*-chlorocinnamate, thence by addn. of  $Br_2$  to give ethyl  $\beta$ -(*p*-chlorophenyl)- $\alpha,\beta$ -dibromopropionate, followed by elimination of 2 HBr and saponification (or vice versa) with alc. KOH, and final acidification (yield not stated), see (1) ]

$\bar{C}$  with  $Cu(OAc)_2$  loses  $CO_2$  yielding (1) *p*-chlorophenylacetylene (3:0590) (cf. also under *o*-chlorophenylpropionic acid (3:2956))

3:4265 (1) Wilson, Wenzke, *J. Am. Chem. Soc.* **57**, 1265-1267 (1935).

3:4270 4,4'-DICHLOROBENZOPHENONE  $C_{13}H_8OCl_2$  Beil. VII - 420  
(Di-*p*-chlorophenyl ketone) VII<sub>1</sub>-(228)



M.P. 148°	(1)	B.P. 353° at 767 mm. (2)
147.75°	(2) (20)	243° at 38 mm. (15)
147°	(19)	
146.5-147.5° cor.	(40)	
146°	(3) (37)	
146°	(4) (5) (6)	
	(7) (8) (16)	
144-145°	(9) (10)	
144.5°	(11) (14)	
144°	(12)	
142-143°	(13) (22)	

Colorless lfts. from alc; eas. sol. ether, acetone, AcOH,  $CHCl_3$ ,  $CS_2$  — [For f.p./compn. data on systems  $\bar{C}$  + benzophenone (1:5150) and  $\bar{C}$  + diphenylamine see (12).]

[For prepn. of  $\bar{C}$  from *p*-chlorobenzoic acid (3:4940) + chlorobenzene (3:7903) +  $AlCl_3$  (82% yield (1)) or from *p*-chlorobenzoyl chloride (3:6550) + chlorobenzene (3:7903) +  $AlCl_3$  in  $CS_2$  in direct sunlight (yields: 90% (17), 75-80% (2), 36% (9)) (37) (some isomeric 2,4'-dichlorobenzophenone (3:1565) also being formed) see indic. refs.; from chlorobenzene (3:7903) +  $AlCl_3$  +  $CO_2$  at 80-150° and 10 atm. press. (*p*-chlorobenzoic acid is main prod.) see (18); from *p*-chlorophenyl  $MgCl$  +  $CO_2$  (together with *p*-chlorobenzoic acid) see (8).]

[For prepn. of  $\bar{C}$  from dichloro-*bis*-(*p*-chlorophenyl)methane (4,4'-dichlorobenzophenone

dichloride) (see below) by hydrolysis with boilg. dil. alc. (14) or conc.  $\text{H}_2\text{SO}_4$  (14) (15) (6) (19) see indic. refs.; from tetra-(*p*-chlorophenyl)ethylene glycol (see below) on fusioo or oo boilg. with AcOH see (20); from 4,4'-dibromobenzophenoone with  $\text{PCl}_5$  at  $150^\circ$  see (21); from 4,4'-dichloro-3-nitrobenzophenoone (see below) via reduction to amioe, diazotizatioo, and treatmeot with  $\text{SOCl}_2 + \text{NaOH}$  see (21).]

[For formn. of  $\bar{\text{C}}$  by oxidation with  $\text{CrO}_3/\text{AcOH}$  of 4,4'-dichlorobenzilic acid (2), of bis-(*p*-chlorophenyl)metbone (7), of tris-(*p*-chlorophenyl)methane (16), of 1,1,4,4-tetra-(*p*-chlorophenyl)butyne-2 (91% yield (4)), or of 1,1,4,4-tetra-(*p*-chlorophenyl)butatriene-1,2,3 (94% yield (5)) see indic. refs.; from oxido. of  $\beta,\beta$ -di-(*p*-chlorophenyl)ethanol with aq.  $\text{KMnO}_4$  see (10); from (*p,p'*-dichlorobenzohydril)pinacolooe . . . . . (p-chlorophenyl)propioophenone by oxidn. with aq.  $\text{KMnO}_4$  in NaOH + pyridine soln. see (13); from bis-(*p*-chlorophenyl)methyleneacetophenoone with  $\text{KMnO}_4$  in acetone (71% yield) see (3).]

[For formn. of  $\bar{\text{C}}$  from 1,1-di-(*p*-chlorophenyl)ethane (3:0995) (39), from 1-chloro-2,2-bis-(*p*-chlorophenyl)ethylene (3:1430) (81% yield (40)), or from 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (3:2438) (40), all by oxidn. with  $\text{CrO}_3/\text{AcOH}$ , see indic. refs.]

[ $\bar{\text{C}}$  on reduction with 3% Na/Hg in 90% alc. (20), with Al/Hg in 80% alc. (6) (11), with Zn dust + AcOH on boilg. (20), with Zn dust + alc. KOH (20) or NaOH (23), or simply with boilg. alc. KOH (24) gives (yields: 100% (23), 96% (6) (11)) di-(*p*-chlorophenyl)carbinol (4,4'-dichlorobenzhydrol) [Beil. VI-680, VI<sub>1</sub>-(327)], cryst. from alc., m.p.  $04^\circ$  (20),  $03^\circ$  (24),  $91.5^\circ$  (23),  $89-90^\circ$  (6) (11) (corresp. 3,5-dinitrobenzoate, m.p.  $174-176^\circ$  (41)); note that in some cases this main prod. is accompaied by tetra-(*p*-chlorophenyl)ethylene glycol (see below). —  $\bar{\text{C}}$  on reduction with Zn dust + AcOH + dil.  $\text{H}_2\text{SO}_4$  (25), or in alc. in bright sunlight for 5 days (20) cf. (26), gives (85% yield (20)) tetra-(*p*-chlorophenyl)ethylene glycol [Beil. VI-1058, VI<sub>1</sub>-(523)], m.p.  $180^\circ$  (6) (11),  $175^\circ$  (20) (accompanied by smaller amts. of other prods.).]

[ $\bar{\text{C}}$  with sodium phenylacetylene in dry ether gives (57% yield (3)) bis-(*p*-chlorophenyl)-ethynyl-carbiol, m.p.  $163-164^\circ$  (3);  $\bar{\text{C}}$  with diphenylmethyl sodium gives (27) bis-(*p*-chlorophenyl)-diphenylmethyl-carbinol, m.p.  $183-184^\circ$  (27);  $\bar{\text{C}}$  with  $\text{MeMgI}$  in dry ether gives (39) (19) not only some bis-(*p*-chlorophenyl)-methyl-carbinol, m.p.  $67.0-68.5^\circ$  (39), but also (68% yield (19)), by loss of  $\text{H}_2\text{O}$ , unsym.-di-(*p*-chlorophenyl)ethylene, m.p.  $91^\circ$  (3:2475);  $\bar{\text{C}}$  with  $\beta$ -(diphenylvinyl)MgBr gives (12% yield (28)) 1,1-di-(*p*-chlorophenyl)-3,3-diphenylpropen-2-ol-1, m.p.  $85^\circ$ , which on btg. at  $130-150^\circ$  loses  $\text{H}_2\text{O}$  yieldiog 1,1-di-(*p*-chlorophenyl)-3,3-diphenylpropadiene-1,2, m.p.  $93-95^\circ$  (28);  $\bar{\text{C}}$  with ethyl bromoacetate + Zn in  $\text{C}_6\text{H}_6$  gives (30% yield (28)) ethyl  $\beta,\beta$ -di-(*p*-chlorophenyl)- $\beta$ -hydroxypropionate, m.p.  $102^\circ$  (28).]

[ $\bar{\text{C}}$  with  $\text{PCl}_5$  nt  $150^\circ$  gives (17) (15) (29) dichloro-di-(*p*-chlorophenyl)metbane (4,4'-dichlorobenzophenoone dichloride), m.p.  $52-53^\circ$  (15),  $52.5^\circ$  (17).]

[ $\bar{\text{C}}$  oo fusioo with NaOH yields (7) chlorobenzene (3:7903) + *p*-chlorobenzoic acid (3:4940). —  $\bar{\text{C}}$  with 10% aq. NaOH in pres. of Cu 5 hrs. at  $190^\circ$  uoder press. yields (30) 4,4'-dihydroxybenzophenoone [Beil. VIII-317, VIII<sub>1</sub>-(641)], m.p.  $214^\circ$  (30).]

[ $\bar{\text{C}}$  with hydrazine hydrate in isopropyl alc. in s.t. at  $150-160^\circ$  for 7 hrs. gives (56% yield (42)) 4,4'-dichlorobenzophenoone hydrazone, m.p.  $91-93^\circ$ , which on Wolff-Kishner reduction gives (21% yield (42)) 4,4'-dichlorodiphenylmethane (3:1057).]

[ $\bar{\text{C}}$  with aq.  $\text{NH}_4\text{OH}$  in pres. of CuO +  $\text{NH}_4\text{NO}_3$  +  $\text{KClO}_3$  under press. at  $180^\circ$  (1) ef. (31) gives (92% yield (1)) 4,4'-diaminobenzophenoone [Beil. XIV-88, XIV<sub>1</sub>-(391)], m.p.  $245-246^\circ$  (1),  $242.5^\circ$  (31); some half reactn. prod., viz., 4-amino-4'-chlorobenzophenoone, m.p.  $185^\circ$  (1), is also formed. — For similar reactn. of  $\bar{\text{C}}$  with diethylamine leadiog to 4-chloro-4'-diethylaminobenzophenoone see (32). — For reactn. of  $\bar{\text{C}}$  with *N*-methyl- $\alpha$ -

phenylindole and use in prepn. of dyes see {33}; with ethylhutyl-*m*-toluidine see {34}; with aminoanthraquinone derivs. see {35} {36}.]

[ $\bar{C}$  on nitration with 10 wt. pts. fuming  $\text{HNO}_3$  ( $D = 1.47$ ) in cold {37} or with 5 pts. abs.  $\text{HNO}_3$  at  $0^\circ$  {2} gives (81% yield {37}) 4,4'-dichloro-3,3'-dinitrobenzophenone, cryst. from AcOH, m.p.  $132.5^\circ$  {2},  $132-133^\circ$  {38},  $120^\circ$  {37};  $\bar{C}$  on trinitration at  $130^\circ$  with 1.8 wt. pts. conc.  $\text{H}_2\text{SO}_4$  contg. 2 pts.  $\text{KNO}_3$  gives {37} 4,4'-dichloro-3,3',5-trinitrobenzophenone, cryst. from AcOH, m.p.  $140^\circ$  {37};  $\bar{C}$  on tetranitration with 10 pts. fuming  $\text{H}_2\text{SO}_4$  + 1 pt.  $\text{KNO}_3$  at  $150^\circ$  gives {37} 4,4'-dichloro-3,3',5,5'-tetranitrobenzophenone, cryst. from AcOH, m.p.  $202^\circ$  {37}.] [A mono-nitrated  $\bar{C}$ , viz., 4,4'-dichloro-3-nitrobenzophenone, ndls. from alc., m.p.  $87^\circ$  {2},  $88-89^\circ$  {38} has been obt'd. indirectly.]

④ 4,4'-Dichlorobenzophenone oxime: ndls. from alc., m.p.  $136-136.5^\circ$  {1},  $136^\circ$  {7},  $135^\circ$  {8} {9},  $134^\circ$  {5}. [From  $\bar{C}$  with excess  $\text{NH}_2\text{OH}$  in alc. at  $100^\circ$  {9}] [This prod. by Beckmann rearr. with conc.  $\text{H}_2\text{SO}_4$  yields *p*-chlorobenz-*p*-chloroanilide, m.p.  $213-213.5^\circ$  {1}.]

— 4,4'-Dichlorobenzophenone phenylhydrazone: not reported.

— 4,4'-Dichlorobenzophenone *p*-nitrophenylhydrazone: not reported.

— 4,4'-Dichlorobenzophenone 2,4-dinitrophenylhydrazone: m.p.  $238-240^\circ$  {40}.

3:4270 {1} Newton, Groggins, *Ind. Eng. Chem.* 27, 1397-1399 (1935). {2} Montagne, *Rec. trav. chim.* 21, 24-29 (1902). {3} Meyer, Schuster, *Ber.* 55, 822-823 (1922). {4} Brand, Horn, Bausch, *J. prakt. Chem.* (2) 127, 246-247 (1930). {5} Brand, Bausch, *J. prakt. Chem.* (2) 127, 235-236 (1930). {6} Cohen, Böeseken, *Rec. trav. chim.* 38, 115-116, 123 (1919). {7} Stephen, Short, Gladding, *J. Chem. Soc.* 117, 623 (1920). {8} Bodroux, *Bull. soc. chim.* (3) 31, 29 (1904). {9} Dittrich, *Ann.* 264, 175-178 (1891). {10} Fuson, Kozacik, Eaton, *J. Am. Chem. Soc.* 55, 3803 (1933).

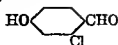
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{31} Britton, Bryner (to Dow Chem. Co.), U.S. 1,946,058, Feb. 6, 1934; *Cent.* 1934, I 3396; *C.A.* 28, 2364 (1934). {32} Hammond, Harris (to Heyden Chem. Co.), U.S. 2,223,517, Dec. 3, 1940; *C.A.* 35, 1808 (1941). {33} Wolf (to I.G.), *Brit.* 417,014, Oct. 25, 1934; *Ger.* 604,429, Oct. 20, 1934; *French* 761,372, March 17, 1934; *Swiss* 170,094, Sept. 11, 1934; *Cent.* 1935, I 801. {34} Wolf, *Chem. Abstr.* 1935, 1000. {35} Wolf, *Chem. Abstr.* 1935, 1000. {36} Wolf, *Chem. Abstr.* 1935, 1000. {37} Wolf, *Chem. Abstr.* 1935, 1000. {38} Wolf, *Chem. Abstr.* 1935, 1000. {39} Wolf, *Chem. Abstr.* 1935, 1000. {40} Wolf, *Chem. Abstr.* 1935, 1000.

*J. Am. Chem. Soc.* 67, 1599, 1602 (1945).

{11} Grummitt, Buck, *J. Am. Chem. Soc.* 67, 693-694 (1945). {42} Grummitt, Jenkins, *J. Am. Chem. Soc.* 68, 914 (1946).

3:4280 2-CHLORO-4-HYDROXYBENZ-  
ALDEHYDE $C_7H_5O_2Cl$  Beil. VIII - 81  
VIII<sub>1</sub>—

M.P. 147-148° (1)

146.5° (2)

Colorless ndls. from AcOH (1) or aq. (2). — Volatile with steam but much less so than the isomeric 4-chloro-2-hydroxybenzaldehyde (3:0960) (1).

[For prepn. of  $\bar{C}$  from *m*-chlorophenol (3:0255) via Reimer-Tiemann reactn. see (1); via anhyd. HCN +  $AlCl_3$  +  $C_6H_6$  (50% yield) see (2); for prepn. (alm. 100% yield (1)) from 2-chloro-4-nitrotoluene via 2-chloro-4-aminotoluene and subsequent diazo reactn. see (1).]

$\bar{C}$  does not reduce  $NH_4OH/AgNO_3$  or Fehling soln. (1).

$\bar{C}$  with aq.  $FeCl_3$  gives only a slight ppt. [dif. from 4-chloro-2-hydroxybenzaldehyde (3:0960)]; the copper and chromium salts are lighter green in color than those from that isomer (1).

$\bar{C}$  on mononitration as specified (3) yields 5-nitro-2-chloro-4-hydroxybenzaldehyde, vol. with steam, colorless ndls. from alc., m.p. 125° (3). [This product yields a phenylhydrazone, silky dark purple ndls. from alc., m.p. 166° sl. dec.; a *p*-nitrophenylhydrazone, deep or. ndls. from AcOH, m.p. 266° dec.; and a semicarbazone, light or. ndls. from dil. AcOH, m.p. 266° dec. (3).]

$\bar{C}$  on dinitration as specified (3) yields 3,5-dinitro-2-chloro-4-hydroxybenzaldehyde, not volatile with steam, pale yel. massive pr. from aq., m.p. 93° (3). [This product yields a phenylhydrazone, br.-purple ndls. from alc., m.p. 210° dec.; a *p*-nitrophenylhydrazone, red-br. ndls. from dil. AcOH, m.p. 267° dec.; and a semicarbazone, lt. br. ndls. from dil. AcOH, m.p. 192° dec. (3).]

② 2-Chloro-4-hydroxybenzaldehyde: cryst. from alc., m.p. 194° (2).

— 2-Chloro-4-hydroxybenzaldehyde phenylhydrazone: unrecorded.

③ 2-Chloro-4-hydroxybenzaldehyde *p*-nitrophenylhydrazone: dark red pl. from alc. or vermilion red cryst. from AcOH, m.p. 288° dec. (1).

— 2-Chloro-4-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.

④ 2-Chloro-4-hydroxybenzaldehyde semicarbazone: yel. cryst. from alc., m.p. 214° (1).

⑤ 2-Chloro-4-acetoxybenzaldehyde: colorless ndls. from dil. AcOH, m.p. 51.5° (1).

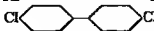
⑥ 2-Chloro-4-benzyoxybenzaldehyde: colorless ndls. from alc., m.p. 96.5° (1). [Note that this ⑥ does not give good distinction from isomeric 4-chloro-2-hydroxybenzaldehyde (3:0960) whose corresponding benzoate has m.p. 98.5° (1).]

3:4280 (1) Hodgson, Jenkinson, *J. Chem. Soc.* 1927, 1740-1742. (2) Gattermann, *Ann.* 357, 334 (1907). (3) Hodgson, Jenkinson, *J. Chem. Soc.* 1923, 2274-2275.

## 3:4300 4,4'-DICHLOROBIPHENYL

 $C_{12}H_8Cl_2$ 

Beil. V - 579

V<sub>1</sub>-(273)V<sub>2</sub>-(484)

M.P. 148-149° cor. (1) (2)

147.5-148.5° (3)

148°

(4) (5) (6) (7)

(8) (15) (17)

147-148°

(9) (10) (18)

146.5-147°

(11)

144-145°

(12)

B.P. 315-319° (13)

315°

(15) (17)

Colorless cryst. from toluene + lt. pet. (2), from 50% AcOH (14), or from alc. (11).

[For prepn. of  $\bar{C}$  from 4,4'-diaminobiphenyl (benzidine) [Beil. XIII-214, XIII<sub>1</sub>-(58)] via tetrazotization and use of Cu powder (9), Cu<sub>2</sub>Cl<sub>2</sub> (3), or HgCl<sub>2</sub> complex (82% yield (10)), see indic. refs.; from biphenyl (1:7175) in AcOH with Cl<sub>2</sub> (41% yield (2)) (convenient for prepn. small amts  $\bar{C}$ ) see (2); from 4,4'-dinitrobiphenyl with SOCl<sub>2</sub> in s. t. for 10 hrs. at 200-210° see (7); from *p*-chloriodobenzene [Beil. V-221, V<sub>1</sub>-(119)] with Cu powder at 200-250° (82% yield) see (15).]

[For formn. of  $\bar{C}$  from chlorobenzene (3:7903) by pyrolysis see (16) (12) (for discussion of formn. during mfg. of phenol from chlorobenzene see (19)); from biphenyl (1:7175) with Cl<sub>2</sub> in pres. of SbCl<sub>5</sub> (17) or I<sub>2</sub> (13) see indic. refs.; from 4,4'-dihydroxybiphenyl (1:1640) with PCl<sub>5</sub> see (13); from 4,4'-dichlorobiphenyl-3,3'-dicarboxylic acid on htg. see (18); from 4,4'-dichloro-3,3'-diaminobiphenyl via tetrazotization and htg. with alc. see (14), from decompn. of bis-(*p*-chlorobenzoyl) peroxide on htg. see (6).]

[For manuf. of  $\bar{C}$  or mixts. of dichlorobiphenyls contg.  $\bar{C}$  from biphenyl with Cl<sub>2</sub> see (20) (21) (22) (23); for use as insecticide see (24) ]

$\bar{C}$  htd. under press. with conc. aq. NH<sub>4</sub>OH in pres. of Cu<sub>2</sub>Cl<sub>2</sub> and Ca(OH)<sub>2</sub> gives (99.5% yield (25)) 4,4'-diaminobiphenyl (benzidine);  $\bar{C}$  with aq. over Cu + silica gel at 525-600° gives (26) 4,4'-dihydroxybiphenyl (1:1640).]

$\bar{C}$  on mononitration in 15 pts. AcOH with 10 pts. HNO<sub>3</sub> (*D* = 1.46) nt 100° for ½ hr. (2), or in nitrobenzene soln. with HNO<sub>3</sub> (*D* = 1.52) as directed (2), gives alm. quant. yield of 4,4'-dichloro-2-nitrobiphenyl, cryst. from alc. or CCl<sub>4</sub>, m.p. 102° (2) (27). [This prod. does not react with piperidine (27) ]

$\bar{C}$  on dinitration by soln. in 7½ pts. HNO<sub>3</sub> (*D* = 1.52) in an ice bath gives (2) mixt. contg. 81.3% 4,4'-dichloro-2,3'-dinitrobiphenyl and 18.7% 4,4'-dichloro-2,2'-dinitrobiphenyl. By recryst. from AcOH 4,4'-dichloro-2,3'-dinitrobiphenyl is obtd. in ndls., m.p. 141-142° (2), 140° (28), which on warming with piperidine for a few seconds yields (28) 4-chloro-4'-piperidino-2,3'-dinitrobiphenyl, or. ndls. from alc., m.p. 132° (28) (note that the principal dinitration prod. of  $\bar{C}$  is the 2,3'-dinitro- $\bar{C}$  and not the 2,2'-isomer as formerly (29) supposed). — From the mother liq. of the above dinitration may be obtd. (2) the true 4,4'-dichloro-2,2'-dinitrobiphenyl, m.p. 138-139° (2); this does not react with piperidine.

$\bar{C}$  on trinitration with 10 pts. HNO<sub>3</sub> (*D* = 1.52) for 2 hrs. at 100° gives (2) (30) 4,4'-dichloro-2,3',5'-trinitrobiphenyl, ndls. from AcOH, m.p. 166-167° (2), 164-165° (30); this prod. warmed with piperidine gives 4-chloro-4'-piperidino-2,3',5'-trinitrobiphenyl, crimson pr. from AcOH, m.p. 182° (2).

$\bar{C}$  on oxida. with CrO<sub>3</sub> in AcOH yields (13) *p*-chlorobenzoic acid (3:4940), m.p. 237° (13).

3:4300 (1) Williamson, Rodebush, *J. Am. Chem. Soc.* 63, 3019 (1911). (2) Shaw, Turner, *J. Chem. Soc.* 1932, 288-289, 294-296. (3) Bretscher, *Helv. Phys. Acta* 1, 358 (1928). (4) Griess, *J. Chem. Soc.* 20, 101 (1867). (5) *Helv. Chim. Acta* 9, 285 (1926). (6) Fichter, Adler, *Helv. Chim. Acta* 65, 24 (1933). (7) Bröll, *Gazz. chim. ital.* 63, 24 (1933). (8) *Helv. Chim. Acta* 59, 870 (1929). (9) *Helv. Chim. Acta* 59, 870 (1929). (10) Schwegler, *Ber.* 65, 1607 (1932). (11) Pickett, Walter, France, *J. Am. Chem. Soc.* 58, 2296 (1936). (12) Meyer, Hofmann, *Monatsh.* 38, 143 (1917). (13) Schmidt, Schultz, *Ann.* 207, 338-344 (1881). (14) Hodgson, Holt, *J. Chem. Soc.* 1934, 1432. (15) Ullmann, *Ann.* 332, 54-55 (1901). (16) Kramers, *Ann.* 189, 137-140 (1877). (17) Kramers, *Ann.* 189, 142-145 (1877). (18) Schultz, Rohde, Vicari, *Ann.* 352, 130 (1907). (19) Hale, Britton, *Ind. Eng. Chem.* 20, 122 (1923). (20) Malowan (to Swann Research, Inc.), U.S. 1,951,577, March 20, 1934; *Cent.* 1934, II 3183; C.A. 28, 3427 (1934).

(21) Federal Phosphorus Co., French 703,216, April 27, 1931; *Cent.* 1931, II 1635. (22) Britton, Stoecker (to Dow Chem. Co.), U.S. 1,835,754, Dec. 8, 1931; *Cent.* 1932, I 1110. (23) Prahl, Mathes (to F. Raschig), Ger. 580,512, July 13, 1933; *Cent.* 1933, II 1763. (24) I.G.,



Ger. 513,775, Dec. 2, 1930; *Cent.* 1931, I 1965. (25) Booth (to Swann Research, Inc.), U.S. 1,954,469, April 10, 1934; *Cent.* 1934, II 1846; *C.A.* 28, 3744 (1934); Federal Phosphorus Co., Brit. 370,774, May 4, 1932; *Cent.* 1932, II 1237. (26) Booth (to Swann Research, Inc.), U.S. 1,925,367, Sept. 5, 1933; *Cent.* 1934, I 128; *C.A.* 27, 5342 (1933). (27) LeFevre, Turner, *J. Chem. Soc.* 1926, 2045 (28) Dennett, Turner, *J. Chem. Soc.* 1926, 477, 479-480. (29) Borsche, Scholten, *Ber.* 50, 609 (1917). (30) Vernon, Rebernak, Ruwe, *J. Am. Chem. Soc.* 54, 4456-4457 (1932).

## 3:4315 6,7-DICHLORONAPHTHOL-1

 $C_{10}H_6OCl_2$ 

Beil. VI-613

VI<sub>1</sub>—VI<sub>2</sub>—

M.P. 151° (1) (2)

149-150° (3)

Cryst. from  $CHCl_3$  (3).

[For prepn. from  $\beta$ -(3,4-dichlorobenzal)propionic ac. [Beil. IX-614] by distn. see (1) (2) (3);  $\bar{C}$  is sepd. from the smaller proportion of 7,8-dichloronaphthol-1 (3:2635) by the greater soly. of the latter in lgr. (3).]

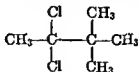
$\bar{C}$  on oxidn. with  $K_2Cr_2O_7$  + dil.  $H_2SO_4$  yields (3) 4,5-dichlorophthalic ac. (3:4890), which during m.p. detn. is converted to 4,5-dichlorophthalic anhydride (3:4830), m.p. 184-185° (3).

$\bar{C}$  in alk. soln. coupled with diazotized naphthionic acid (1-aminonaphthalenesulfonic acid-4) gives a deep red-bluish color which upon acidification becomes dark yellow (3). [Dif. from 7,8-dichloronaphthol-1 (3:2635) q.v.]

Ⓔ 6,7-Dichloro-1-naphthyl acetate: ndls. from dil. alc., or compact pr. from  $CHCl_3$  lgr., m.p. 102-103° (3).

3:4315 (1) Armstrong, Wynne, *Chem. News* 71, 253 (1895). (2) Armstrong, Wynne, *Proc. Chem. Soc.* 11, 78-79 (1895); *Ber.* 29, Referate, 223-224 (1896). (3) Erdmann, Schwedten, *Ann.* 275, 286-288 (1893).

## 3:4325 3,3-DICHLORO-2,2-DIMETHYLBUTANE

 $C_6H_{12}Cl_2$ 

Beil. I - 150

I<sub>1</sub>—I<sub>2</sub>-(113)

M.P. 151-152° (1)

Colorless cryst. subliming readily even at ord. temp.

[For prepn. of  $\bar{C}$  from *ter*-butyl methyl ketone (pinacolone) (1:5425) with  $PCl_5$  at 0-5° (1) (2) (3) (4) (5) (6) (7) (9) see indic. refs. Note that  $\bar{C}$  (by loss of HCl) is always accompanied by more or less 3-chloro-2,2-dimethylbutene-3 (3:7340) and other prods.]

$\bar{C}$  on btg. with phenol + KOAc yields (8) 3-chloro-2,2-dimethylbutene-3 (3:7340).

$\bar{C}$  on btg. at 150-230° with powdered KOH (moistened with alc.) gives (65% yield (6)) (9) (2) *ter*-butylacetylene [Beil. I-256], b.p. 37.8° at 760 mm.,  $D_4^{20} = 0.6683$ ,  $n_D^{20} = 1.37257$  (3); note that use of NaOH instead of KOH gives by loss of 1 HCl only 3-chloro-2,2-dimethylbutene-3 (3:7340) and no *ter*-butylacetylene (9).

3:4325 (1) Bartlett, Rosen, *J. Am. Chem. Soc.* 64, 544 (1942). (2) Delacre, *Bull. soc. chim.* (3) 35, 343-344 (1906). (3) Favorskii, *J. Russ. Phys.-Chem. Soc.* 19, 425 (1887); *Ber.* 20, Referate 781 (1887). (4) Delacre, *Bull. acad. roy. Belg.* 1906, 7-41; *Cent.* 1906, I 1233-1234. (5) Delacre, *Cent.* 1906, II 496. (6) Ivitzky, *Bull. soc. chim.* (4) 35, 357-358 (1924). (7) Meerwein, Wortman, *Ann.* 435, 201, Note 4 (1924). (8) Meerwein, Wortman, *Ann.* 435, 194, Note 1 (1924). (9) de Graef, *Bull. soc. chim. Belg.* 34, 428-429 (1925).

## 3:4330 2-CHLORONAPHTHOIC ACID-1


 $C_{11}H_7O_2Cl$  Beil. IX-651  
IX<sub>1</sub>—

M.P. 152-153° (1)

151-152° (2)

151° (4)

Cryst. from  $C_6H_6$  (2). — Sol. in 1000 pts. aq. at 20° or in 126 pts. aq. at 100°; eas. sol. alc., ether (1).

[For prepn of  $\bar{C}$  from 2-hydroxynaphthoic acid-1 [Beil. X-328, X<sub>1</sub>-(144)] with  $PCl_5$  (3 moles) in s.t. at 180-190° for 8 hrs. followed by treatment with aq. see (1) (2); from 1-chloroformylnaphthyl-2-phosphonic acid dichloride [Beil. X-329] with  $PCl_5$  (2 moles) in s.t. at 180-190° followed by treatment with aq. see (1) (2); from 2-chloro-1-(chloromethyl)-naphthalene (4) by oxidn. with dil  $HNO_3$  for 15 days see (4).]

$\bar{C}$  in aq. susp. with 2% Na/Hg yields (1)  $\alpha$ -naphthoic acid (1:0785), m.p. 160° (1).

$\bar{C}$  does not esterify upon treatment in MeOH with HCl gas (3).

Salts:  $Ca\bar{A}_2 \cdot 2H_2O$ ; sol. in 150 pts. cold aq. or 75 pts. hot aq.; loses water of hydration completely at 180° (1).

⊗ Methyl 2-chloro-1-naphthoate: pr. from alc. + toluene, m.p. 50° (1) (2), b.p. 176-180° at 18.5 mm. (2). [From  $Ag\bar{A}$  with MeI in s.t. at 100° (1) or from  $\bar{C}$  with ethereal diazomethane (2).] [This ester is very resistant to hydrolysis (1) (2)]

— Ethyl 2-chloro-1-naphthoate: unreported.

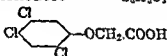
— *p*-Bromophenacyl 2-chloro-1-naphthoate: unreported.

3:4330 (1) Rabe, *Ber.* 22, 394-396 (1889). (2) Bergmann, Hirschberg, *J. Chem. Soc.* 1936, 333-334. (3) Meyer, *Ber.* 23, 184 (1895). (4) Horn, Warren, *J. Chem. Soc.* 1916, 144.

## 3:4335 2,4,5-TRICHLOROPHENOXYACETIC ACID

 $C_8H_5O_3Cl_3$ 

Beil. S.N. 522



M.P. 153° (1)

Colorless cryst. from  $C_6H_6$ ; alm. insol. aq. — Neut. Eq. = 255.5.

[For prepn of  $\bar{C}$  from 2,4,5-trichlorophenol (3:1620) with chloroacetic acid (3:1370) in aq. NaOH (85% yield) see (1).]

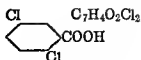
[For use of  $\bar{C}$  as weed killer see (2); for general survey of activity of  $\bar{C}$  as plant hormone see (4) (5)]

[For prepn. of ethylene glycol bis-(2,4,5-trichlorophenoxyacetate), m.p. 140°, and its use as plasticizer see (3).]

3:4335 (1) Pokorny, *J. Am. Chem. Soc.* 63, 1768 (1941). (2) Hamner, Tukey, *Science* 100, 151-155 (1945). (3) G. H. Hamner, *Science* 100, 151-155 (1945). (4) G. H. Hamner, *Science* 100, 151-155 (1945). (5) G. H. Hamner, *Science* 100, 151-155 (1945).

Am. Soc. Hort. Sci. 50, 107-108 (1947), Can. J. 22, 4313 (1945).

## 3:4340 2,5-DICHLORO BENZOIC ACID

 $C_7H_4O_2Cl_2$ 

Beil. IX - 342

IX<sub>1</sub>-(141)

M.P. 155°	(1)	153°	(7) (8)	B.P. 301° (12)
154.5°	(2)	152°	(9)	
154.4°	(3)	151-152°	(10)	
154°	(4) (21)	150°	(11)	
153.5°	(5)	149-150°	(12)	
153.0-153.5°	(6)	147-148°	(13)	

Ndls. from aq. or dil. alc. — Somewhat volatile with steam. — Sol. in 1193 pts. aq. at 11° (12); in 1177 pts. at 14° (11).

[For prepn. of  $\bar{C}$  from 2,5-dichlorotoluene (3:6245) by hgt. with dil.  $HNO_3$  in s.t. at 140° (60% yield (4)) (5) (13) (2) (8) (7) or hgt. with  $KMnO_4$  (14) see indicated refs.; for prepn. of  $\bar{C}$  from 2,5-dichlorobenzaldehyde (3:1145) via Cannizzaro reactn. (84% yield (1)) see (1) (4); for prepn. (90-95% yield (9)) from 5-chloro-2-aminobenzoic acid via diazo reactn +  $CuCl$  see (9) (11); from 2,5-dichloroaniline via 2,5-dichlorobenzonitrile (m.p. 130°) and its hydrolysis with fung.  $HCl$  at 180° see (15); for prepn. of  $\bar{C}$  from benzoic acid +  $KClO_3$  +  $HCl$  see (12) (21); for still other misc. methods see Beil. IX-342, IX<sub>1</sub>-(141).]

For f.p./compn. data on mixtures of  $\bar{C}$  with *m*-chlorobenzoic acid, m.p. 154.4° (3:4392), and with 2,3-dichlorobenzoic acid, m.p. 154.4° (3:4650), see (2).

$\bar{C}$  on hgt. with 3 pts. conc.  $H_2SO_4$  + 2 pts. aq. loses  $CO_2$  at 220° yielding *p*-dichlorobenzene (3:0980) (5).

The direct nitration of  $\bar{C}$  is unrecorded. [However, 2,5-dichloro-3-nitrobenzoic acid, ndls. from  $AcOH$ , m.p. 220°, and 2,5-dichloro-6-nitrobenzoic acid [Beil. IX-404], m.p. 143-144°, have both been prepd. by oxidn. (16) of the corresp. aldehydes.]

$\bar{C}$  with  $PCl_5$  (17) or with  $SOCl_2$  (18) yields 2,5-dichlorobenzoyl chloride, h.p. 137° at 15 mm. (17), 95.3-95.5° at 1 mm. (18). [For formn. in chlorination of benzoyl chloride see (2)]

— Methyl 2,5-dichlorobenzoate: unrecorded.

— Ethyl 2,5-dichlorobenzoate: b.p. 271° cor. (12). [For study of hydrolysis see (20).]

④ 2,5-Dichlorobenzamide: woolly ndls. from aq., m.p. 155° (12).

⑤ 2,5-Dichlorobenzanilide: from 2,5-dichlorobenzoyl chloride (above) + aniline (11), pr. from  $C_6H_5$ , m.p. 240° (11).

⑥ 2,5-Dichlorobenz-3-nitroanilide: from 2,5-dichlorobenzoyl chloride (above) + *m*-nitroaniline (19), ndls. from aq.  $MeOH$ , m.p. 151-152° u.c. (19).

3:4340 (1) Lock, *Ber.* 66, 1531 (1933). (2) Hope, Riley, *J. Chem. Soc.* 123, 2470-2480 (1923). (3) Bornwater, Holleman, *Rec. trav. chim.* 31, 227-230 (1912). (4) de Crauw, *Rec. trav. chim.* 50, 773 (1931). (5) Lellmann, Klotz, *Ann.* 231, 319 (1885). (6) Gassmann, Hartmann, *J. Am. Chem. Soc.* 63, 2394 (1941). (7) Cohen, Dakin, *J. Chem. Soc.* 79, 1130 (1901). (8) Turner, Wynne, *J. Chem. Soc.* 1936, 712. (9) Eller, Klemm, *Ber.* 55, 222 (1922). (10) Twiss, Farinholt, *J. Am. Chem. Soc.* 58, 1564 (1936).

(11) Hübner, *Ann.* 222, 201-203 (1883). (12) Beilstein, *Ann.* 179, 290-293 (1875). (13) Feldmann, Kopeliowitsch, *Arch. Pharm.* 273, 491 (1935). (14) Ullmann, Wagner, *Ann.* 371, 117 (1911).

356. (20) Blakey, McCombie, Scarborough, *J. Chem. Soc.* 1926, 2863-2868.

(21) Biswas, Das-Gupta, *J. Indian. Chem. Soc.* 19, 497-498 (1942); *C.A.* 37, 5709 (1943).

3:4355 2-CHLORO-4-METHYLBENZOIC  
ACID $C_8H_7O_2Cl$ Beil. IX-497  
IX<sub>1</sub>—

M.P. 155.0-155.5° u.c. (1)

149-150° (2)

Colorless ndls. from alc.; spar. sol. cold, more sol. bot. aq.; eas. sol. alc., ether,  $CHCl_3$ , hot  $C_6H_6$ .

[For prepn. of  $\bar{C}$  from 3-chloro-4-isopropyl-1-methylbenzene (3-chloro-*p*-cymene) (3.8770) by oxidn. with 15 pts. boilg.  $HNO_3$  ( $D = 1.24-1.29$ ) (other products are also formed) see (2), from 3-chloro-4-methylbenzonitrile, m.p. 61-62° (1), by hydrol. with boilg. aq.  $KOH$  (100% yield) see (1).]

Salts.  $NH_4\bar{A}$ ,  $K\bar{A}$ ,  $Na\bar{A} \cdot H_2O$ , all very eas. sol. both in aq. and in alc. (1);  $Ca\bar{A}_2 \cdot 2H_2O$ ,  $Ba\bar{A}_2 \cdot 5H_2O$ , eas. sol. hot aq. (1),  $Ag\bar{A}$ , spar. sol. cold aq. but eas. sol. hot aq. (1).

[ $\bar{C}$  on mononitration by soln. in fuming  $HNO_3$  ( $D = 1.5$ ) at ord. temp. followed by stdg. several hrs. ppts. 2-chloro-5-nitro-4-methylbenzoic acid [Beil. IX-503], cryst. from hot aq. or alc., m.p. 180° u.c. (1), 180-181.5° u.c. (3), 180-181° (4) (note that the isomeric 2-chloro-3-nitro-4-methylbenzoic acid [Beil. IX-503], m.p. 192° u.c. (3), may be formed from  $\bar{C}$  under certain conditions (3)).]

[ $\bar{C}$  on dinitration with mixt. of 1 pt. fuming  $HNO_3$  ( $D = 1.52$ ) + 4 pts. conc.  $H_2SO_4$  gives (3) either in cold or on htg. exclusively 2-chloro-3,5-dinitro-4-methylbenzoic acid [Beil. IX-506], ndls. from alc., m.p. 233° u.c. (3).]

— Ethyl 2-chloro-4-methylbenzoate: oil, b.p. not reported;  $D_4^{21.4} = 1.1591$  (5),  $n_D^{21.4} = 1.52443$  (5)

— 2-Chloro-4-methylbenzamide: ndls. from alc., m.p. 182° (1) [From partial alk. hydrolysis of 2-chloro-4-methylbenzonitrile (see above) (1).]

3:4355 (1) Claus, Davidsen, *J. prakt. Chem.* (2) **39**, 491-496 (1889). (2) Fioleti, Crosa, *Gazz. chim. ital* **16**, 288-290 (1886). (3) Claus, Davidsen, *Ann* **265**, 345-346, 348-349 (1891). (4) Fioleti, Crosa, *Gazz. chim. ital* **18**, 312 (1888). (5) von Auwers, Harres, *Z. physik. Chem.* **A-143**, 18 (1929)

3:4375 *p*-CHLOROPHENOXYACETIC  
ACID $C_8H_7O_3Cl$ 

Beil. VI-187

VI<sub>1</sub>—  
VI<sub>2</sub>-(177)

M.P. 156.7-157.2° cor.

155-156°

151°

(6)

(1) (4) (5)

(2) (3)

Pr. (from hot aq.). — Spar. sol. cold aq.

[For prepn. from *p*-chlorophenol (3:0475) by htg. with chloroacetic ac. (3:1370) and aq. alk. see (1) (4) (5) (6).]

$\bar{C}$  htd. with conc.  $HCl$  in s.t. at 150° yields *p*-chlorophenol (3:0475) (3)

$\bar{C}$  refluxed with 1½ pts. thionyl chloride for 1½ hrs. gives (90% yield) *p*-chlorophenoxyacetyl chloride, b.p. 142° at 17 mm, m.p. 18.8° (1).

The methyl ester (b.p. 177-180°) and the ethyl ester, ndls. (from alc.), m.p. 49°, have been prepared from the acid chloride (1)

*p*-Chlorophenoxyacetamide: from the acid chloride by treatment with excess  $(NH_4)_2CO_3$ ; ndls. from alc., m.p. 133° (1).

*p*-Chlorophenoxyacetanilide: from the acid chloride by action of aniline (2 moles) in  $C_6H_6$ ; ndls. (from nlc.), m.p. 125° (1).

3:4375 (1) Minton, Stephen, *J. Chem. Soc.* 121, 1599-1601 (1922). (2) Michael, *Am. Chem. J.* 9, 216 (1887). (3) Peratoner, *Gazz. chim. ital.* 23, I 239 (1898). (4) Behaghel, *J. prakt. Chem.* 114, 297-298 (1926). (5) Koelsch, *J. Am. Chem. Soc.* 53, 304-305 (1931). (6) Hayes, Branch, *J. Am. Chem. Soc.* 65, 1555-1564 (1943).

### 3:4390 4-CHLOROPHTHALIC ACID



$C_8H_5O_4Cl$  Beil. IX - 816  
IX<sub>1</sub>-(366)

M.P. 157°	(1)
156°	(2)
151°	(3)
150-150.5°	(4)
150° in s.t.	(5)
148° u.c.	(6)

[See also 4-chlorophthalic anhydride (3:2725).]

Ndls. from alc.; cryst. from  $C_6H_6$  or  $CCl_4$ . — Eas. sol. aq., alc., ether, or AcOH.

[For prepn. of  $\bar{C}$  from 4-chlorophthalic anhydride (3:2725) by warming with aq. or from dimethyl 4-chlorophthalate (3) or diethyl 4-chlorophthalate (5) by hydrol. with alk. see indio. refs.; from neutral sodium phthalate in aq. alk. on treatment with  $Cl_2$  see (3) (7) (8) (9) (10); from 4-chloro-2-methylbenzoic acid (3:4700) (11) (12), from 5-chloro-2-methylbenzoic acid (3:4670) (11), from 4-chloro-2-methylacetophenone [Beil. VII-306] (2), or from 7-chloro-1,2,3,4-tetrahydronaphthalene (1) by oxidn. with alk.  $KMnO_4$  see indio. refs.; from 6-chloroindanone-1 [Beil. VII-361] on evapn. with hot 25%  $HNO_3$  see (4); from 1,6-dichloronaphthalene (3:0810) (13), 2,6-dichloronaphthalene (3:4040) (14) (6), 2,7-dichloronaphthalene (3:3445) (14), 6-chloronaphthol-2 (3:3500) (6), or 4-chloro-2-methylbenzoic acid (above) (12) on oxidn. with dil.  $HNO_3$  in s.t. as directed see indio. refs.; from the trichloride of 4-sulphthalic acid [Beil. XI-407] with  $PCl_5$  in s.t. at 220° followed by KOH hydrolysis of the 4-chlorophthalyl (di)chloride see (15); from 4-sulphthalic anhydride (16) by hgt. with  $HCl + NaClO_3$  see (16).]

$\bar{C}$  on hgt. above m.p. gives 4-chlorophthalic anhydride (3:2725).

[ $\bar{C}$  on fusion with KOH (11) or with NaOH at 165-175° (10) gives (100% yield (10)) 4-hydroxyphthalic acid [Beil. X-499, X<sub>1</sub>-(255)], m.p. 204-205°, with conv. to corresp. anhydride, m.p. 171° (note that this same prod. is also obt'd. from the isomeric 3-chlorophthalic acid (3:4820)).]

[ $\bar{C}$  htd. under press. nt 350° with aq. + cat. loses  $CO_2$  presumably yielding (17) *m*-chlorobenzoic acid (3:4392) and/or *p*-chlorobenzoic acid (3:4940).]

[ $\bar{C}$  with  $NH_3$  gas + cat. as directed (18) yields 4-chlorophthalonitrile, m.p. 130-132° (19).]

[For use of  $\bar{C}$  as softener for cellulose derivatives see (20); for reaction of  $\bar{C}$  with naphthalene +  $AlCl_3$  yielding intermediates for vat dyes see (21).]

$\bar{C}$  on hgt. with resorcinol + few drops conc.  $H_2SO_4$ , then dissolving in alk., gives fluorescein reactn. (2). —  $\bar{C}$  is unstable toward  $KMnO_4$  (2).

Salts.  $Ba\bar{A}$ ,  $Ca\bar{A}$ , dif. sol. aq.;  $Ba\bar{A} \cdot H_2\bar{A}$ , spar. sol. even in hot aq. (11) (for table of heavy metal salts see (22)).

Esters. Dimethyl 4-chlorophthalate; from  $Ag_2\bar{A}$  with MeI (15), from 4-chlorophthalyl (di)chloride (above) with MeOH (15), or from  $\bar{C}$  in MeOH with  $HCl$  gas (3); ndls. from

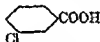
lgr., m.p. 38° (3), 37° (15), b.p. 186-187° at 32 mm. (3); diethyl 4-chlorophthalate; from  $\bar{C}$  in alc. with HCl gas (15) or from diethyl 4-aminophthalate via diazotization and use of  $Cu_2Cl_2$  reactn. (70% yield (5)), b.p. 300-305° (15), 185-190° at 25 mm. (5), 173-174° at 16 mm. (1).

3:4390 (1) von Braun, Larbig, Kredel, *Ber.* 56, 2337-2338 (1923). (2) Mayer, Albert, Schön, *Ber.* 65, 1297 (1932). (3) Ayling, *J. Chem. Soc.* 1929, 253-256. (4) Miersch, *Ber.* 25, 2116 (1892). (5) Blucke, Smith, *J. Am. Chem. Soc.* 51, 1869 (1929). (6) Claus, Dehne, *Ber.* 15, 320-321 (1882). (7) Moore, Marrack, Proud, *J. Chem. Soc.* 119, 1788-1789 (1921). (8) Egerer, Meyer, *Monatsh.* 34, 81-83 (1913). (9) Scottish Dyes, Ltd., Beckett, Bangham, Thomas, *Brit.* 348,632, June 11, 1931; *Cent.* 1931, II 1194 (10) Rushchinskiĭ, *Compt. rend. acad. sci. (U.R.S.S.)* 1933, 118-121; *Cent.* 1935, I 1617.

(11) Krüger, *Ber.* 18, 1758-1759 (1885). (12) Claus, Stapelberg, *Ann.* 274, 289 (1893). (13) Cleve, *Bull. soc. chim.* (2) 29, 499 (1878). (14) Alén, *Bull. soc. chim.* (2) 36, 433-434 (1881). (15) Rée, *Ann.* 233, 237-238 (1886). (16) Waldmann, Schwenk, *Ann.* 487, 290-291 (1931). (17) Jaeger (to Selden Co.), U.S. 1,953,231, Apr. 3, 1934; *Cent.* 1934, II 1688. (18) Imperial Chem. Ind., Ltd., French 766,944, July 6, 1934; *Cent.* 1934, II 2749 (19) Soc. Chem. Ind. Basel, French 844,567, July 27, 1939, *C.A.* 34, 7299 (1940). (20) Dreyfus, French 749,792, July 29, 1933; *Cent.* 1934, I 3154.

(21) B.A.S.F., French 599,039, Dec. 31, 1925; *Cent.* 1926, I 2850. (22) Ephraïm, *Ber.* 55, 3482 (1922).

3:4392 *m*-CHLOROBENZOIC  
ACID


 $C_7H_5O_2Cl$ 

Beil. IX - 337  
IX<sub>1</sub>-(139)

M.P. 159°	(105)	154.5°	(11) (12)
158°	(1) (2) (3)	154.4°	(13)
157.5°	(3) (4)	154.25°	(14)
157°	(5)	154-155°	(15)
156.2°	(6)	154°	(16) (17) (18) (60)
155-156° cor.	(7)	153-154°	(24)
156°	(26)	153.5°	(19)
155°	(8)	153°	(20) (21) (26) (28) (35)
154.8-155.0° cor.	(62)		(70) (84)
154.9°	(8)	152°	(22) (47)
154.8-154.9°	(9)		
154.8°	(10)		

Pr. from hot aq., 30% AcOH or  $C_6H_6$ . —  $\bar{C}$  is spar. sol. cold aq., e.g., 1 pt.  $\bar{C}$  is sol. at 0° in 2840 pts. aq. (23); 100 ml. satd. aq. soln. at 25° conts. 0.0385 g.  $\bar{C}$  (60). —  $\bar{C}$  is eas. sol. hot aq., alc., ether. — At 14-16° C 100 ml. of satd. soln. of  $\bar{C}$  in ether conts. 14 g.  $\bar{C}$ ; in  $C_6H_6$ , 0.66 g.  $\bar{C}$ ; in  $CS_2$ , 0.62 g.  $\bar{C}$ ; in  $CCl_4$ , 0.08 g.  $\bar{C}$  (8). — For study of soly. of  $\bar{C}$  in  $C_6H_6$  or *n*-heptane see (11); in chlorobenzene (3:7903), in *o*-chlorotoluene (3:8245), or in *m*-chlorotoluene (3:8275) see (10); in acetone or  $C_6H_6$  see (6); for soly. of  $\bar{C}$  in aq. solns. of various salts including NaA see (60). — For distribution coefficients of  $\bar{C}$  at 25° between aq. + toluene or between aq. and  $CHCl_3$  see (102).

$\bar{C}$  can be sublimed under reduced press. (24) (14). —  $\bar{C}$  is but very slightly volatile with steam (for details see (12)). — For study of adsorption of  $\bar{C}$  by charcoal from acetone or  $C_6H_6$  soln. see (6).

Binary systems contg.  $\bar{C}$ : [For f.p./compn. data on system  $\bar{C}$  +  $H_2O$  see (25). — For f.p./compn. data and diagram of system  $\bar{C}$  + benzoic acid (1:0715) (eutectic, m.p. 96.0° (20), 95.4° (27) (8), contg. 36 wt. %  $\bar{C}$  (27) (20) (8) (28)) see indic. refs. — For f.p./compn. data on systems  $\bar{C}$  + *m*-toluic acid (1:0705) (26),  $\bar{C}$  + *m*-hydroxybenzoic acid (1:0825) (26), see indic. refs.]

[For f.p./compo. data on system  $\bar{C}$  + *o*-chlorobenzoic acid (3:4150) (eutectic, m.p. 110.7°, cootg. 47-48 mole %  $\bar{C}$  (20) (27) (8) (19)) see indic. refs.; on system  $\bar{C}$  + *p*-chlorobenzoic acid (3:3940) (eutectic, m.p. 140.9°, cootg. 80 mole %  $\bar{C}$  (8) (19) cf. (104)) see indic. refs.; on system  $\bar{C}$  + 2,5-dichlorobenzoic acid (3:4340) (eutectic, m.p. 119.7°, cootg. 51-58 mole %  $\bar{C}$ ) see (13).]

[For f.p./compo. data on systems  $\bar{C}$  + *o*-bromobenzoic acid (28),  $\bar{C}$  + *m*-bromobenzoic acid (28),  $\bar{C}$  + *p*-bromobenzoic acid (28), *m*-iodobenzoic acid (29), *o*-nitrobenzoic acid (30), *m*-nitrobenzoic acid (30) see indic. refs.]

Ternary systems contg.  $\bar{C}$ : [For influence of addn. of benzoic acid (20) or of *p*-chlorobenzoic acid (3:4940) (27) to eutectic of  $\bar{C}$  with *o*-chlorobenzoic acid (3:4150) see indic. refs. — For influence of addn. of *o*-chlorobenzoic acid (3:4150) to eutectic of  $\bar{C}$  with benzoic acid (1:0715) see (27); for data on system  $\bar{C}$  + *o*-chlorobenzoic acid (3:4150) + *p*-chlorobenzoic acid (3:4940) see (19).]

Miscellaneous. [For study of fate of  $\bar{C}$  in animal organism see (31) cf. (102) (note that although from man  $\bar{C}$  is excreted (34) as *N*-(*m*-chlorobenzooyl)glycine (*m*-chlorohippuric acid) [Beil. IX-339], m.p. 143-144° (31), yet from dog and rabbit no evidence for this conjugation product has been found (31). — For study of use of  $\bar{C}$  as a preservative see (32). — For use of  $\bar{C}$  as vulcanization regulator see (33).]

Preparation. [For prepo. of  $\bar{C}$  from benzoic acid (1:0715) by chlorination with  $Cl_2$  (38) in pres. of  $FeCl_3$  (70% yield (8)), with  $KClO_3$  + conc.  $HCl$  (35) (36) (37) (38), with aqua regia at 100° (yield 32% (39)) (7), with  $SbCl_5$  (35) (40) (84), with  $MoO_3$  + conc.  $HCl$  in s.t. at 150° (41), with  $NaOCl$  soln. (20) (42), or with  $Ca(OCl)_2$  soln. (42) (35) (38) see indic. refs. (note that in all these cases numerous other chlorination products are also formed); from cinnamic acid (1:0735) by chlorination and oxidn. with  $Ca(OCl)_2$  soln. see (35) (38).]

[For prepo. of  $\bar{C}$  by oxidn. of *m*-chlorotoluene (3:8275) with  $K_2Cr_2O_7$  +  $H_2SO_4$  (43), with 5% aq.  $KMoO_4$  (75% yield (4)) (8), with dil.  $HNO_3$  in s.t. at 130-140° for 8 hrs. (47), or in aq. alk. at 260° under press. with air (44) see indic. refs.; from 3-chlorobiphenyl (3:8940) or from 3,3'-dichlorobiphenyl (3:0180) by oxidn. with  $CrO_3/AcOH$  in pres. of  $V_2O_5$  see (45); from *m*-chlorobenzaldehyde (3:6475) by oxidn. with alk.  $KMoO_4$  see (3).]

[For prepn. of  $\bar{C}$  from *m*-chlorobenzal (di)chloride (3:6710) by hydrolysis with aq. followed by  $KMoO_4$  oxidn. (7% yield (2)) or from its mixt. with *m*-chlorobenzotrichloride (3:6845) by hydrolysis with 70%  $H_2SO_4$  or 80%  $AcOH$  or 5%  $NaOH$  at 90-100° in stream of air to effect immediate oxidn. (46) see indic. refs.]

[For prepo. of  $\bar{C}$  from *m*-chlorobenzonitrile [Beil. IX-339], m.p. 40.5° (48), by hydrolysis with conc.  $H_2SO_4$  (3), from *N*-(*m*-chlorobenzooyl)glycine (*m*-chlorohippuric acid) by hydrolysis with  $HCl$  (35) (36), see indic. refs.]

[For prepo. of  $\bar{C}$  from *m*-aminobenzoic acid [Beil. XIV-383, XIV-1(558)] via diazotization and use of  $Cu_2Cl_2$  reacto. (74% yield (101)) (3) (4) (49); from *m,m'*-diazaminobenzoic acid (diazaminobenzoic-3,3'-dicarboxylic acid) [Beil. XVI-727] with warm conc.  $HCl$  (50) see indic. refs.]

[For formn. of  $\bar{C}$  from *m*-chloroiodobenzene [Beil. V-220, V-1(167)] by reaction with *n*-butyllithium in ether followed by carbonation with  $CO_2$  (41.5% yield (51)); from *p*-chloronitrobenzene [Beil. V-243, V-1(129), V-1(182)] with alc.  $KCN$  in s.t. at 200° (52); from 3-chlorophthalic acid (3:4820) or 4-chlorophthalic acid (3:4390) by cat. partial decarboxylation (53); from 3-chlorophthalic acid by mercuration and treatment with  $HCl$  (99) see indic. refs.]

Chemical behavior. [ $\bar{C}$  (as  $Na\bar{A}$ ) on reduction in boilg. aq. soln. with  $Na/Hg$  yields (36) (54) benzoic acid (1:0715) (for study of reduction of  $\bar{C}$  with  $H_2$  +  $Ni$  in aq. alk. at ord. temp. see (55));  $\bar{C}$  on electrolytic reduction in alc./ $H_2SO_4$  yields (56) *m*-chlorobenzyl

alcohol [Beil. VI-444], oil, b.p. 234° (56); note that  $\bar{C}$  with Ni/Al alloy (Raney nickel) in aq. alk. soln. at 90° gives (100% yield (106)) benzoic acid (1:0715), m.p. 121°.]

$\bar{C}$  behaves normally as a monobasic acid: e.g.,  $\bar{C}$  on titration with standard dil. aq. alk. gives Neut. Eq. 156.5; ionization const. at 25° is  $1.55 \times 10^{-4}$  (57),  $1.53\text{--}1.59 \times 10^{-4}$  (58),  $1.506 \times 10^{-4}$  (59) cf. (1) (60). — [For study of acid strength of  $\bar{C}$  in MeOH, EtOH, and various other alcs. see (61) (62) (63) (16) (64) (65) (17).]

Salts of inorganic bases.  $[\text{NH}_4\bar{A}]$ , m.p. 203–204° dec. (39), lfts. from acetone/pet. ether (39), powder from abs. alc. (66). — Hydroxylamine salt, ndls. from xylenc, m.p. 144° (72), 145–146° dec. (39). —  $\text{Na}\bar{A}$  (67),  $\text{K}\bar{A}$  (67) both behave as liquid cryst. on fusion. —  $\text{Ag}\bar{A}$ , insol. aq. (68) (note that this salt (1 mole) with  $\text{I}_2$  (2 equiv.) in dry  $\text{C}_6\text{H}_6$  refluxed 15–18 hrs. yields (69) phenyl *m*-chlorobenzoate, m.p. 53°, +  $\text{CO}_2$  +  $\text{AgI}$ ). —  $\text{Ca}\bar{A}_2 \cdot 3\text{H}_2\text{O}$ , sol. at 12° in 82.6 pts. aq. (68) (35). —  $\text{Ba}\bar{A}_2 \cdot 4\text{H}_2\text{O}$ , eas. sol. nq. or alc. (for use in sepn. of  $\bar{C}$  from *o*-chlorobenzoic acid (3:4150) and *p*-chlorobenzoic acid (3:4940) see (27)). —  $\text{Cd}\bar{A}_2 \cdot 2\text{H}_2\text{O}$  (71).]

Salts of organic bases. E.g.,  $\bar{C}$  with equiv. nmt. benzylamine in boilg. EtOAc followed by evapn. of solvent yields (73) benzylammonium *m*-chlorobenzoate, m.p. 146.8–147.4° u.c., 149.2–149.8° cor. (73), Neut. Eq. 263.6 (note that the m.p. of this salt is only very slightly lower than that of the corresp. salt from *o*-chlorobenzoic acid (3:4150)). —  $\bar{C}$  similarly treated with  $\alpha$ -phenylethylamine yields (73)  $\alpha$ -phenylethylammonium *m*-chlorobenzoate, m.p. 142.0–142.6° u.c., 144.7–145.3° cor. (73), Neut. Eq. 277.6 (note that the m.p. of this salt, although better separated from those of the isomeric acids than the preceding case, is very close to that for the corresp. deriv. of cinnamic acid (1:0735)).

$\bar{C}$  (1 mole) in alc. mixed with codeine (1 mole), m.p. 155°, in alc. htd. several minutes, solvent evaporated, and resulting syrup recrystallized from aq. yields (74) codeine *m*-chlorobenzoate,  $\text{C}_{18}\text{H}_{21}\text{O}_5\text{N} \cdot \bar{C}$ , m.p. 96° on "Maquenne block"; note that this m.p. although very close to that (99°) of corresp. salt from *m*-bromobenzoic acid is widely different from the corresp. salts of *o*-chlorobenzoic acid (3:4150) and *p*-chlorobenzoic acid (3:4940), which are 134° and 162° respectively. —  $\bar{C}$  (1 mole) in alc. (or  $\text{CHCl}_3$ ) with strychnine (1 mole) in alc. boiled for a few minutes then cooled yields (75) strychnine *m*-chlorobenzoate,  $\text{C}_{21}\text{H}_{22}\text{O}_5\text{N}_2 \cdot \bar{C}$ , m.p. 185° u.c. on "Maquenne block"; note that this m.p. is somewhat higher than that (170°) of the corresp. salt from *o*-chlorobenzoic acid (3:4150) and widely different from that (251°) of the corresp. salt of *p*-chlorobenzoic acid (3:4940).

$\bar{C}$  with alcohols gives by conventional procedures the corresp. esters; for details on methyl *m*-chlorobenzoate (3:6670) and on ethyl *m*-chlorobenzoate (3:6770) see these compds. — [For study of rate of esterification of  $\bar{C}$  with MeOH (76) or with cyclohexanol (77) see indic. refs.]

$\bar{C}$  with  $\text{P}_2\text{O}_5$  in toluene boiled for 4 hrs. (78) or  $\bar{C}$  with oxalyl (di)chloride (3:5060) refluxed in  $\text{C}_6\text{H}_6$  (79) cf. (80) yields *m*-chlorobenzoic acid anhydride, pl. from  $\text{C}_6\text{H}_6$  or toluene, ndls. from lt. pet. or alc., m.p. 95.5° (78), 95° (79) (note that  $\bar{C}$  (2 moles) with oxalyl (di)bromide refluxed in  $\text{C}_6\text{H}_6$  similarly gives good yields (80) of the above anhydride but  $\text{Na}\bar{A}$  with oxalyl dibromide can also be used (80) to prepare *m*-chlorobenzoyl bromide, oil, b.p. 143–147° at 40 mm. (80)).

$\bar{C}$  with  $\text{PCl}_5$  (31) (68) (3) or with  $\text{SOCl}_2$  (81) (82) or with  $\text{SOCl}_2$  + pyridine (83) gives (76% yield (31)) *m*-chlorobenzoyl chloride (3:6590), b.p. 225°.

$\bar{C}$  with  $\text{HN}_3$  in conc.  $\text{H}_2\text{SO}_4$  in trichloroethylene (3:5170) soln. at 40° gives (75% yield (107)) *m*-chloroaniline.]

$\bar{C}$  fused with KOH, subsequently acidified, yields (81) *m*-hydroxybenzoic acid (1:0825).

$\bar{C}$  on nitration with boilg. fuming  $\text{HNO}_3$  for 10 min. (70) or with abs.  $\text{HNO}_3$  at 0° or –20° (3) (21) (85) gives a mixt. of two isomeric nitro-*m*-chlorobenzoic acids; this mixt. consists mainly (92–93% (86) cf. (21)) of 3-chloro-6-nitrobenzoic acid [Beil. 1X-401],



cryst. from  $\text{HNO}_3$  ( $D = 1.1$ ) (24), ether,  $\text{C}_6\text{H}_6$ , or aq., m.p.  $139^\circ$  (85),  $137\text{--}138^\circ$  (70),  $136^\circ$  (3),  $135\text{--}136^\circ$  (24), accompanied by a little (7–8% (86)) cf. (24) 3-chloro-2-nitrobenzoic acid [Beil. IX-400], ndls. or thls. from hot aq., m.p.  $235^\circ$  (70) (85),  $233\text{--}234^\circ$  (3) (for details on sepn. of these two isomers see (3) (70) (24) (85)). — Note that the other two possible nitro-*m*-chlorobenzoic acids are known but are not found in the product from nitration of  $\bar{\text{C}}$ ; they are 3-chloro-4-nitrobenzoic acid [Beil. IX-404], m.p.  $185\text{--}186^\circ$ , and 3-chloro-5-nitrobenzoic acid [Beil. IX-403, IX<sub>1</sub>-(165)], m.p.  $147^\circ$ . — [Note also that no dinitro-3-chlorobenzoic acids have ever been reported.]

— Methyl *m*-chlorobenzoate: b.p.  $231^\circ$ , m.p.  $21^\circ$ . (See 3:6670.)

— Ethyl *m*-chlorobenzoate: b.p.  $245^\circ$ . (See 3:6770.)

① *p*-Nitrobenzyl *m*-chlorobenzoate: m.p.  $107.2^\circ$  u.c. (87). [From  $\bar{\text{C}}$  (as  $\text{Na}\bar{\text{A}}$ ) with *p*-nitrobenzyl bromide (m.p.  $99^\circ$ ) in boilg. dil. alc. (87); note that m.p. of this ester is almost identical with that ( $106^\circ$  (83)) of the corresp. ester of *o*-chlorobenzoic acid (3:4150).]

② Phenacyl *m*-chlorobenzoate: m.p.  $118^\circ$  (89),  $116.4^\circ$  (21). [From  $\bar{\text{C}}$  (as  $\text{Na}\bar{\text{A}}$ ) with phenacyl bromide (m.p.  $50^\circ$ ) in boilg. alc. (98% yield (21)).]

— *p*-Chlorophenacyl *m*-chlorobenzoate: unreported.

③ *p*-Bromophenacyl *m*-chlorobenzoate: m.p.  $117.2^\circ$  (21),  $116^\circ$  (90). [From  $\bar{\text{C}}$  (as  $\text{Na}\bar{\text{A}}$ ) with *p*-bromophenacyl bromide (m.p.  $109^\circ$ ) in boilg. alc. (21).]

— *p*-Iodophenacyl *m*-chlorobenzoate: unreported.

④ *p*-Phenylphenacyl *m*-chlorobenzoate: m.p.  $154^\circ$  u.c. (91). [From  $\bar{\text{C}}$  (as  $\text{Na}\bar{\text{A}}$ ) with *p*-phenylphenacyl bromide (m.p.  $126^\circ$ ) in boilg. alc. (91); note that the m.p. of this deriv. is only slightly lower than that ( $160^\circ$  u.c. (91)) of the corresp. ester of *p*-chlorobenzoic acid (3:4940); note also that, since this ester has almost the same m.p. as the original  $\bar{\text{C}}$ , care must be taken to show that the supposed ester is insol. in aq.  $\text{Na}_2\text{CO}_3$  (dif. and sepn. from  $\bar{\text{C}}$ ); note finally that the m.p. of a mixt. of  $\bar{\text{C}}$  with this ester is depressed to  $130\text{--}132^\circ$  (91).]

⑤ *S*-Benzylthiuronium *m*-chlorobenzoate: cryst. from alc., m.p.  $155^\circ$  cor. (92). [From  $\text{Na}\bar{\text{A}}$  or  $\text{K}\bar{\text{A}}$  in dil. alc. with slight excess *S*-benzylthiuronium chloride soln. (15% in hot alc.) (92).]

⑥ *S*-(*p*-Chlorobenzyl)thiuronium *m*-chlorobenzoate: cryst. from dioxane, m.p.  $157^\circ$  cor. (93). [From  $\text{Na}\bar{\text{A}}$  or  $\text{K}\bar{\text{A}}$  in aq. with 1 equiv. of *S*-(*p*-chlorobenzyl)thiuronium chloride, m.p.  $197^\circ$  (10% in alc.) (93); note that the m.p. of this prod. is closely adjacent to that (m.p.  $159^\circ$  cor. (93)) of the corresp. salt of *o*-chlorobenzoic acid (3:4150), and is also almost identical with that of the original  $\bar{\text{C}}$ .]

⑦ *S*-(*p*-Bromobenzyl)thiuronium *m*-chlorobenzoate: m.p.  $150^\circ$  cor. (94). [From  $\text{Na}\bar{\text{A}}$  or  $\text{K}\bar{\text{A}}$  in aq. with 1 equiv. of *S*-(*p*-bromobenzyl)thiuronium bromide, m.p.  $213^\circ$ , in alc. (94).]

⑧ *m*-Chlorobenzamide: cryst. from hot aq. or alc., m.p.  $135^\circ$  (100),  $134.5^\circ$  cor. (3),  $134^\circ$  u.c. (95),  $132\text{--}133^\circ$  (70). [From *o*-chlorobenzoyl chloride (3:6590) with conc. aq.  $\text{NH}_4\text{OH}$  (68) (70) or from  $\bar{\text{C}}$  by refluxing with  $\text{AcOH} + (\text{NH}_4)_2\text{CO}_3$  (46–50% yield (100)); note that this amide gives on fusion with  $\text{HgO}$  a mercuric deriv., m.p.  $245^\circ$  u.c. (95).]

⑨ *m*-Chlorobenzhydrazide: ndls. from aq. or alc., m.p.  $158^\circ$  (96),  $157\text{--}158^\circ$  (97). [From ethyl *m*-chlorobenzoate (3:6770) with hydrazine hydrate in abs. alc. on 8-hr. reflux. (yield: 97% (96), 87% (97)).] — [For use of *m*-chlorobenzhydrazide as general reagent for identification of aldehydes and ketones see (97).]

— *N'*-(*m*-Chlorobenzoyl)-*N*-phenylhydrazide: unreported.

— *m*-Chlorobenzanilide: *cryst. from alc.*, m.p. 122–125° (98). [Prepn. reported but only by indirect means (98).] — [Note that the isomeric *benz-m-chloroanilide* [Beil. XII-605] has m.p. 118°.]

— *m*-Chlorobenzo-*p*-toluidide: unreported.

— *m*-Chlorobenzo- $\alpha$ -naphthalide: unreported.

— *m*-Chlorobenzo- $\beta$ -naphthalide: unreported.

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**3:4395 2-CHLORO-3-HYDROXYBENZOIC ACID**



$C_7H_5O_3Cl$

Beil. X - 142

X<sub>1</sub>—

M.P. 157.5-158.5° (1)  
 156.5-157.5° (1)  
 150-157° (2) (5)  
 156° (3)  
 155.0-155.5° u.c. (10)

Colorless lfts. from aq. or  $C_6H_6$ . [Ioniz. const. at 25° =  $1.40 \times 10^{-3}$  (5).]

[For prepn. of  $\bar{C}$  from 2-chloro-3-hydroxybenzaldehyde (3:4085) with 5-6 pts. 50% KOH at 60-70° (Cannizzaro reactn.) (96% yield) see (3); from ethyl 2-chloro-3-hydroxybenzoate (see below) by hydrolysis with 35% KOH see (1) (2) cf. (4); for formn. from *m*-hydroxybenzoic acid (1:0825) with  $Cl_2$  in MeOH (6) (44% yield (10)) or AcOH (1) (together with some of the isomeric 6-chloro-3-hydroxybenzoic acid (3:4720)) see indic. refs; for prepn. of  $\bar{C}$  from 2-amino-3-hydroxybenzoic acid (1) via diazotization and use of  $Cu_2Cl_2$  reactn. see (1).]

Salts:  $Ag\bar{A}$ , cryst. ppt. (2).

$\bar{C}$  in aq. soln. gives with  $FeCl_3$  a violet-red color.

[ $\bar{C}$  with formalin (1:0145) + conc. HCl + HCl gas at room temp. gives (87% yield (10)) 7-chloro-6-hydroxyphthalide, m.p. 290° cor. (10).]

— Methyl 2-chloro-3-hydroxybenzoate: pr. with 1  $H_2O$  from dil. alc., m.p. 70-71° (2); anhydrous form, m.p. 62-65° (2). [From  $\bar{C}$  in MeOH with  $H_2SO_4$  (2).] — [This ester with MeI + MeOH/KOH in s.t. at 130° for several hours gives methyl 2-chloro-3-methoxybenzoate, anhydrous ndls. from dil. alc., m.p. 41-42° (2).]

— Ethyl 2-chloro-3-hydroxybenzoate: white ndls. with 1  $H_2O$  from dil. alc., m.p. 53° (2); above m.p. loses aq. giving viscous oil (2). [From ethyl *m*-hydroxybenzoate (1:1471) with  $SO_2Cl_2$  (together with the isomeric ethyl 6-chloro-3-hydroxybenzoate (2) (4)).] — [This anhydrous ester with AcCl yields ethyl 2-chloro-3-acetoxybenzoate, ndls. from dil. alc., m.p. 48-49° (2).]

— 2-Chloro-3-methoxybenzoic acid: colorless ndls. from aq., m.p. 161.5° (7), 160° (8) (9). [Prepd. indirectly from 2-chloro-3-methoxybenzaldehyde by oxidn. with  $KMnO_4$  (7) (8).]

— 2-Chloro-3-acetoxybenzoic acid: cryst. from aq. or  $C_6H_6$ , m.p. 152.5–153° u.c.  
(10). [From  $\bar{C}$  +  $Ac_2O$  +  $K_2CO_3$  (10)]

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3:4400 3,5-DICHLORO-4-HYDROXYBENZ-  
ALDEHYDE



$C_7H_4O_2Cl_2$  Beil. VIII - 81  
VIII—

M.P. 158–159° cor. (1)  
156° (2) (3)

Colorless odorless ndls. from dil alc or from  $CHCl_3$ , fairly eas. sol. alc., ether, AcOH; more dif. sol.  $C_6H_6$ , lgr.,  $CHCl_3$

[For prepn. of  $\bar{C}$  from *p*-hydroxybenzaldehyde (1:0060) in 5 pts. AcOH at 100° (2) (4) or in  $CHCl_3$  with cooling (1) with  $Cl_2$  see indic. refs.; from corresp. methyl ether (3,5-dichloro-4-methoxybenzaldehyde) with boulg. conc. HI see (3)]

$\bar{C}$  in *N* KOH with  $H_2O_2$  yields (4) 2,6-dichlorohydroquinone (3:4600).

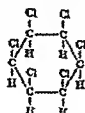
[The methyl ether of  $\bar{C}$  (see above) has been obtd. indirectly (3) from *p*-methoxybenzaldehyde (*p*-anisaldehyde) (1.0240) by chlorination with large excess (9 moles)  $SO_2Cl_2$ ; bright red cryst. from alc., m.p. 61.5° (3); on oxidn. with  $CrO_3$  this prod. gives (80% yield (3)) 3,5-dichloro-*p*-methoxybenzoic acid [Beil. X-177], m.p. 202.0–202.5° (3)]

① 3,5-Dichloro-4-hydroxybenzaldehyde: colorless ndls. from dil. alc., m.p. 185° (2). [From  $\bar{C}$  in moderately conc. NaOH (3 moles) with  $NH_2OH \cdot HCl$  ( $1\frac{1}{2}$  moles), subsequently acidified with AcOH (2).] — [This oxime on boulg. with  $Ac_2O$  for 2 hrs. yields (2) 3,5-dichloro-4-acetoxybenzonitrile, colorless cryst. from dil. alc., m.p. 93° (2).]

② 3,5-Dichloro-4-hydroxybenzaldehyde semicarbazone: greenish yel. ndls. from AcOH, m.p. 236–237° cor. dec. (1) [From  $\bar{C}$  in hot AcOH (50 pts.) by addn. of conc. aq. soln. of semicarbazide hydrochloride, followed by  $\frac{1}{2}$  hr. htg. (1)]

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3:4410 *cis*-1,2,3,4,5,6-HEXACHLORO-  
CYCLOHEXANE  
( $\alpha$ -Benzenehexachloride)



$C_6H_4Cl_6$  Beil. V - 23  
V<sub>1</sub>-(8)  
V<sub>7</sub>-(11)

M.P. 168.2° (1)  
158° (2)  
157° cor. (3) (21)

[See also  $\beta$ -benzenehexachloride (3:4920).]

Nine stereoisomeric configurations of benzenehexachloride are possible (cf. (1)) and four are known;  $\bar{C}$  (contrary to earlier opinion (5)) is now thought (but not unequivocally proved) to have the *cis* configuration; the  $\beta$ -isomer has been shown to have the *trans* configuration; the configurations of the  $\gamma$ -isomer, m.p. 112–113° (2), and the  $\delta$ -isomer, m.p. 129–132° (2), are unknown.

$\bar{C}$  cryst. from 80% AcOH (3) or from alc. —  $\bar{C}$  is volatile with steam (dif. and separation from  $\beta$ -isomer). —  $\bar{C}$  is insol. aq. hut sol. in 22.8 pts.  $\text{CHCl}_3$  at 15.25°; in 15.4 pts.  $\text{C}_6\text{H}_6$  at 18.25° (5). —  $\bar{C}$  forms with the  $\beta$ -isomer a eutectic (m.p. 155.5°) contg. 79.7%  $\bar{C}$  (2).

[For manuf. of ordinary benzenehexachloride (mixt. of stereoisomers) from  $\text{C}_6\text{H}_6$  (1:7400) +  $\text{Cl}_2$  in pres. of light (6) (7) (8), X-radiation (9), or conc.  $\text{H}_2\text{SO}_4$  (10) see indic. refs.; for study of prepn. of  $\bar{C}$  (together with other stereoisomers) from  $\text{C}_6\text{H}_6$  with  $\text{Cl}_2$  in pres. of 1% aq. NaOH see (3) (2) (28), in gas phase (11) (12), in pres. of ethylene in the dark (13), in pres. of  $\text{NCl}_3$  in the dark (14) or in light (15), in pres. of light (16) (17) (18) (19) (20).] [For use of  $\bar{C}$  as insecticide see (27); note, however, that insecticidal props. are thought to be due to  $\gamma$ -isomer (29).]

$\bar{C}$  on htg. above its m.p. loses HCl and yields (3) (21) 1,2,4-trichlorobenzene (3:6420).  $\bar{C}$  on htg. with aq. in s.t. at 200° (19), on boilg. with MeOH/KOH (2), EtOH/KOH (2) (3) (19) (20) (22), alc. KCN (19), or pyridine (2), or on htg. with quinoline at 105–110° (2) yields mainly 1,2,4-trichlorobenzene (3:6420) together with other prods.; e.g.,  $\bar{C}$  on boilg. with excess 10% alc. KOH for  $\frac{3}{2}$  hr. (2) or  $\bar{C}$  boiled with 10 pts. pyridine for 1 hr. (2) gives (yield: 75–86% (2)) 1,2,4-trichlorobenzene (3:6420).

$\bar{C}$  reacts very vigorously with boilg. aniline (19), hut the prods. have not been detd. [ $\bar{C}$  stood in s.t. with 3 pts. liq.  $\text{Cl}_2$  for 11 days yields (23)  $\alpha$ -nonachlorocyclohexane, cryst. from alc., m.p. 95–96° (23) (24).]

$\bar{C}$  in alc. boiled with Zn dust yields (25) benzene (1:7400).

$\bar{C}$  is very inert to most other reagents: e.g.,  $\bar{C}$  can be recrystallized unchanged from fuming  $\text{HNO}_3$  (3), is unattacked by fuming  $\text{H}_2\text{SO}_4$  (19), is unattacked by  $\text{CrO}_3$  (3), is only slightly affected by aq.  $\text{KMnO}_4$  even on boilg. (3), and is unaffected by conc. aq.  $\text{NH}_4\text{OH}$  (3), boilg. alc.  $\text{AgNO}_3$  (3), or  $\text{AgOAc}$  (26).

3:4410 (1) van de Vloed, *Bull. soc. chim. Belg.* 48, 255–256 (1938). (2) van der Linden, *Ber.* 45, 231–247 (1912). (3) Matthews, *J. Chem. Soc.* 59, 165–172 (1891). (4) Williams, Fogelberg, *J. Am. Chem. Soc.* 53, 2103 (1931). (5) Friedel, *Bull. soc. chim.* (3) 5, 130–138 (1891). (6) Hardie (to Imperial Chem. Ind., Ltd.), U.S. 2,218,148, Oct. 15, 1940; *C.A.* 35, 1071 (1941). (7) Imperial Chem. Ind., Ltd., Grant, Brit. 504,569, April 26, 1939; *Cent.* 1939, II 1775; *C.A.* 33, 7822 (1939). (8) Stephenson, Curtis, Brit. 447,058, May 7, 1936; *Cent.* 1936, II 3360; *C.A.* 30, 6766 (1936). (9) Loiseau, French, 565,356, Jan. 25, 1924; *Cent.* 1925, II 1227. (10) Battagay, French 641,102, July 28, 1928; *Cent.* 1928, II 1718.

(11) Lane, Noyes, *J. Am. Chem. Soc.* 54, 161–169 (1932). (12) Lane, Noyes, *J. Am. Chem. Soc.* 55, 4444–4459 (1933). (13) Stewart, Hanson, *J.* (1931). (14) Coleman, Noyes, *J. Am. Chem. Soc.* 43, 2216 (1921). (15) Faraday, *Ann. chim.* (2) 30, 274 (1825).

(16) Faraday, *Ann. chim.* (2) 30, 274 (1825). (17) Faraday, *Ann. chim.* (2) 30, 274 (1825). (18) Leeds, Everhart, *J. Am. Chem. Soc.* 2, 206 (1880). (19) Meunier, *Ann. chim.* (6) 10, 223–269 (1887). (20) Lesimple, *Ann.* 137, 122–124 (1866).

(21) Tei, Komatsu, *Mem. Coll. Sci. Kyoto Imp. Univ.* 10-A, 325–330 (1927); *Cent.* 1928, I 2370; *C.A.* 22, 1086 (1928). (22) Jungfleisch, *Ann. chim.* (4) 15, 270 (1868). (23) van der Linden, *Rec. trav. chim.* 57, 218–221 (1938). (24) Willgerodt, *J. prakt. Chem.* (2) 35, 416 (1887). (25) Zinin, *Zeit. für Chemie* 1871, 284. (26) Griffin, Nelson, *J. Am. Chem. Soc.* 37, 1554 (1915). (27) Bender (to Great Western Electrochem. Co.), U.S. 2,010,841, Aug. 13, 1935; *Cent.* 1936, I 1112. (28) Klingstedt, Wiese, Rüdbeck, *Acta Acad. Aboensis Math. et Phys.* 4, No. 2, 1–36 (1927). (29) Taylor, *Nature* 155, 393–394 (1945).

### 3:4420 4,8-DICHLORONAPHTHOL-2



$\text{C}_{10}\text{H}_6\text{OCl}_2$  Beil. VI —  
VI<sub>1</sub>—  
VI<sub>2</sub>-(604)

M.P. 158–159° (1).


Colorless ndls. from alc. — sol. in NaOH.

[For prepn. from 4,8-dichloronaphthylamine-2 via diazo reaction see (1).]

[For use in prepn. of azo dyestuffs see (2) ]

$\bar{C}$  on suitable methylation yields methyl ether, viz., methyl 2,4-dichloro- $\beta$ -naphthyl ether, colorless ndls., m.p. 93° (1).

3:4420 (1) Friedländer, Karamessinis, Schenk, *Ber.* 55, 48-49 (1922). (2) Herzberg, Wunderlich (to I.G.), Ger. 459,989, May 18, 1928; *Cent.* 1928, II 395.

3:4430 2-CHLORO-4-HYDROXYBENZOIC ACID   $C_7H_5O_3Cl$  Beil. S.N. 1069


M.P. 159° (1)

Colorless ndls. from aq.

[For prepn. of  $\bar{C}$  from 2-chloro-4-methoxybenzoic acid (see below) by cleavage with conc. HI ( $D = 1.7$ ) see (1).]

[The corresp. methyl ether, viz., 2-chloro-4-methoxybenzoic acid (2-chloro-*p*-anisic acid), m.p. 208° (2) (3), has been obtd. indirectly from 2-chloro-4-methoxybenzaldehyde [Beil. VIII-51] (2) or from 2-chloro-4-methoxytoluene [Beil. VI-402] (3) by  $KMnO_4$  oxidn. (2) (3).]

3:4430 (1) Hodgson, Jenkinson, *J. Chem. Soc.* 1927, 1742. (2) Tiemann, *Ber.* 24, 712 (1891). (3) Ullmann, Wagner, *Ann.* 353, 368 (1907).

3:4435 3-CHLORO-2-METHYLBENZOIC ACID   $C_9H_7O_2Cl$  Beil. IX-407  
IX<sub>1</sub>—

M.P. 159° (1)

156° (2)

154° (3)


Colorless ndls from alc; eas. sol. alc.

[For prepn. of  $\bar{C}$  from 3-chloro-2-methylbenzonitrile, m.p. 19° (1), by refluxing with 20% aq. KOH for 5 hrs (98% yield) see (1); from 3-chloro-1,2-dimethylbenzene (3:8645) on oxidn. with boilg<sup>o</sup> dil.  $HNO_3$  ( $D = 1.20$ ) see (3); from 2-methylbenzoic acid (*o*-toluic acid) (1:0690) in  $CHCl_3$  in pres. of Fe with  $Cl_2$  (4) or in AcOH with  $Cl_2$  (2) see indic. refs.]

Salts:  $Ca\bar{A}_2 \cdot 2H_2O$ , spar. sol. hot aq. (3).

$\bar{C}$  on oxidn with  $KMnO_4$  gives (3) 3-chlorophthalic acid (3:4820)

3:4435 (1) Noeltig, *Ber.* 37, 1025-1026 (1904). (2) Claus, Bayer, *Ann.* 274, 310-311 (1893). (3) Krüger, *Ber.* 18, 1758 (1885). (4) Claus, Stapelberg, *Ann.* 274, 311 (1893).

3:4444 3,5,6-TRICHLORO-2-HYDROXYHYDROQUINONE   $C_6H_2O_3Cl_3$  Beil. VI-1089  
VI<sub>1</sub>—  
VI<sub>2</sub>—(1072)

M.P. 160° (1)

Ndls. from  $C_6H_6$  —  $\bar{C}$  cryst. from  $C_6H_6$  or AcOH in solvated form.  $\bar{C}$  is eas. sol. alc., ether; spar. sol. pet. ether.

[For prepn. of  $\bar{C}$  from 3,5,6-trichloro-2-hydroxybenzoquinone-1,4 [Beil. VIII-238] by reduction with aq.  $SO_2$  see (1).]

$\bar{C}$  dis. in aq. yielding colorless soln. which on htg. develops violet color;  $\bar{C}$  with aq. alk. gives deep green color changing to brown (1).

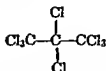
— 3,5,6-Trichloro-2-hydroxyhydroquinone trimethyl ether: unreported.

— 3,5,6-Trichloro-2-hydroxyhydroquinone triethyl ether: unreported.

— 3,5,6-Trichloro-2-hydroxyhydroquinone triacetate: ndls. from lgr./ $C_6H_6$ , m p.  $171^\circ$  (1). [From  $\bar{C}$  with  $Ac_2O + NaOAc$  on htg. (1).]

3:4444 (1) Zincke, Schaum, *Ber.* 27, 557-558 (1894).

3:4450 OCTACHLOROPROPANE  
(Perchloropropane)



$C_3Cl_8$

Beil. I - 108

I<sub>1</sub>- (35)

I<sub>2</sub>-

M.P.  $160^\circ?$  (1) B.P.  $268-269^\circ$  at 734 mm. (1)

White extraordinarily pliable (2) crystals, difficult to filter with suction (because of their high vapor pressure (3)) and best purified by fractional distn. (3) or slow sublimation in vac. (2). — Very sol. in alc., ether, or lgr. (1).

[For prepn. of  $\bar{C}$  (100% yield (3)) from 1,1,1,2,2,3,3-heptachloropropane (3:0200) by conversion with MeOH/KOH by loss of HCl to 1,1,1,2,3,3-hexachloropropene-2 (3:6370) and subsequent treatment with  $Cl_2$  below  $50^\circ$  in sunlight see (3) (2).] [For formn. from 1,2,3-trichloropropane (3:5840) or from isobutyl chloride (3:7135) with excess  $ICl_3$  at  $200^\circ$  see (1).]

$\bar{C}$  on htg. at  $300^\circ$  (1) or on htg. with  $AlCl_3$  (2) splits quantitatively (2) into  $CCl_4$  (3:5100) + tetrachloroethylene (3:5460).

[For fluorination of  $\bar{C}$  see (3) (4); for use of  $\bar{C} + Zn$  for production of smoke see (5) (6)]

3:4450 (1) Krafft, Merz, *Ber.* 8, 1296-1302 (1875). (2) Prins, *J. prakt. Chem.* (2) 89, 416-417 (1914). (3) Henne, Ladd, *J. Am. Chem. Soc.* 60, 2494 (1938). (4) French 730,370, Aug. 11, 1932; French 730,370, Aug. 11, 1932. (5) Métié, *Chimie & industrie*, Spec. No. 179 (1933). (6) Métié, French 649,853, Dec. 28, 1928; *Cent.* 1931, I 311.

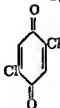
3:4470 2,5-DICHLOROBENZOQUINONE-1,4  
(p-Dichlorobenzoquinone)

$C_6H_2O_2Cl_2$

Beil. VII - 632

VII- (346)

M.P.  $161-162^\circ$  (1)  
 $160.4-161.4^\circ$  (2)  
 $161^\circ$  u.c. (3)  
 $161^\circ$  (4) (17) (28)  
 $159^\circ$  (5) (10)  
 $158.5^\circ$  (6)  
 $158-161^\circ$  (7)



[See also 2,5-dichlorohydroquinone (3:4690).]

Dark yellow cryst. from alc. or  $C_6H_6$ ; insol. aq.; alm. insol. cold dil. alc., eas. sol. hot lgr. abs. alc.; fairly eas. sol. ether or  $CHCl_3$ . — Volatile with steam; sublimes in vacuum.

[For prepn. of  $\bar{C}$  from 2,5-dichlorohydroquinone (3:4690) by oxidn. with  $K_2Cr_2O_7$  or

$\text{Na}_2\text{Cr}_2\text{O}_7$  + dil.  $\text{H}_2\text{SO}_4$  (2) (4) (6) (8) (9) or with conc.  $\text{HNO}_3$  at ord. temp (5) see indic. refs.; from 2,5-dichlorohydroquinone dimethyl ether with fuming  $\text{HNO}_3$  in the cold see (1); from 2-chlorobenzoquinone-1,4 (3:1100) via conversion with  $\text{HCl}$  to 2,5-dichlorohydroquinone (3:4690) and subsequent oxidn. of latter see (5) (17); from 2,5-dichloroaniline [Beil. XII-625, XII-311] with  $\text{CrO}_3$  (5) or from 2,5-dichloro-*p*-phenylenediamine [Beil. XIII-118] with  $\text{CrO}_3$  (10) or  $\text{K}_2\text{Cr}_2\text{O}_7$  + dil.  $\text{H}_2\text{SO}_4$  (28) see indic. refs.; for formn. of  $\bar{C}$  from benzoquinone-1,4 (1:9025) in  $\text{CCl}_4$  with  $\text{ICl}$  on gentle warming. see (3); from benzene with  $\text{ClO}_2$  see (11), from copper salt of quinic acid [Beil. X-535, XI-(270)] by oxidn. with  $\text{MnO}_2$  +  $\text{NaCl}$  +  $\text{H}_2\text{SO}_4$  see (12) ]

[For study of oxidn.-reductn. potential of system  $\bar{C}$  + 2,5-dichlorohydroquinone (3:4690) see (6) (13) (14).] — [For use as vulcanization accelerator see (15); for use in prepn of curdoid dyes see (16), for study of bactericidal actn. see (18).]

$\bar{C}$  is sol in conc.  $\text{H}_2\text{SO}_4$  with greenish-yellow color, in dimethylaniline with deep blue color (10),  $\bar{C}$  is sol in dil. aq. alk. with brown color and decomposition (11) (12).]

$\bar{C}$  with  $\text{KCN}$  in 85%  $\text{MeOH}$  gives (20) a ruby-red soln. with red fluorescence;  $\bar{C}$  with diphenylketene in ether + pet. eth. gives a compound, m.p. 180-192° dec. (21) ]

$\bar{C}$  in aq. reduces with  $\text{SO}_2$  (12) to 2,5-dichlorohydroquinone (3:4690) q.v. (note that the intermediate quinhydrone, dark violet pr. or greenish-black ndls. with 2  $\text{H}_2\text{O}$  (12), crystal water lost over  $\text{H}_2\text{SO}_4$  or on warming giving yellow anhydrous form, m.p. 140-145° (22), is known), however,  $\bar{C}$  in dil. aq.  $\text{NaOH}$  (under  $\text{N}_2$ ) treated with  $\text{SO}_2$  is in part reduced to 2,5-dichlorohydroquinone (3:4690) and in part sulfonated to mono- and disulfonic acids of  $\bar{C}$  (23).

$\bar{C}$  in  $\text{CHCl}_3$  at low temps. does not react with  $\text{Cl}_2$ ; at ord. temps., however, yields tetrachlorobenzoquinone-1,4 (chloranil) (3:4978) (24). —  $\bar{C}$  in  $\text{AcOH}$  at 70-80° with 2 moles  $\text{Br}_2$  gives (alm. quant. yield (4)) (25) (9) 2,5-dichloro-3,6-dibromobenzoquinone-1,4 [Beil. VII-642], golden-brown tbls. from  $\text{C}_6\text{H}_6$ , m.p. 292° (4).]

$\bar{C}$  with conc.  $\text{HCl}$  gives no boilg. (5) 2,3,5-trichlorobenzoquinone-1,4 (3:4672), but some tetrachlorobenzoquinone (chloranil) (3:4978) is also formed.]

$\bar{C}$  (1 pt.) in  $\text{Ac}_2\text{O}$  (5 pts.) +  $\text{AcOH}$  (5 pts.) loses color on boilg. with  $\text{Zn}$  dust (1) and yields (by reductive acylation) 2,5-dichlorohydroquinone diacetate, cryst. from alc., m.p. 141° (1)

$\bar{C}$  (1 pt.) in hot  $\text{AcOH}$  (40 pts.) + conc.  $\text{HCl}$  (0.4-0.5 pt.) treated with aniline (0.4-0.5 pt.) yields mainly (26) 2,5-dichloro-3-anilinobenzoquinone-1,4 [Beil. XIV-137], blue lts., m.p. 180° (26), and 2,5-dichlorohydroquinone (3:4690) accompanied by small amts. of 2,5-dichloro-3,6-dianilinobenzoquinone-1,4 (see below);  $\bar{C}$  htd. with excess aniline yields (26) 2,5-dichloro-3,6-dianilinobenzoquinone-1,4 [Beil. XIV-144], yel.-br. tbls. from  $\text{C}_6\text{H}_6$ , m.p. 290° (26), and 2,5-dichlorohydroquinone (3:4690).

$\bar{C}$  in  $\text{C}_6\text{H}_6$  + alc. warmed with slightly more than 1 mole  $\text{NH}_2\text{OH} \cdot \text{HCl}$  yields (5) (27) 2,5-dichlorobenzoquinone-1,4 monoxime (2,5-dichloro-4-nitrosophenol) [Beil. VII-633], pale yel. cryst. from  $\text{C}_6\text{H}_6$ , m.p. 155-160° (8) (purified by conv. with  $\text{Ac}_2\text{O}$  +  $\text{NaOAc}$  to its acetate, yel. pr. from  $\text{C}_6\text{H}_6$ , m.p. 149° (8), and subsequent hydrolysis with  $\text{NaOH}$ ). —  $\bar{C}$  in alc. with excess  $\text{NH}_2\text{OH} \cdot \text{HCl}$  yields (27) 2,5-dichlorobenzoquinone-1,4 dioxime, grayish yel. cryst. from  $\text{C}_6\text{H}_6$ , m.p. not stated (27) ]

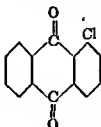
3:4470 (1) Kohn, Gurewitsch, *Monatsh.* 56, 135-136 (1930). (2) Hammick, Hampson, Jenkins, *J. Chem. Soc.* 1934, 1264. (3) Jackson, Bolton, *J. Am. Chem. Soc.* 36, 1454 (1914). (4) Ling, *J. Chem. Soc.* 61, 558-559, 563-566, 572-576 (1892). (5) Levy, Schultz, *Ann.* 210, 150-153 (1881). (6) Conant, Fieser, *J. Am. Chem. Soc.* 45, 2205-2206 (1923). (7) Pfeiffer, *Ann.* 412, 292-293 (1916). (8) Kehrman, Grab, *Ann.* 303, 12-14 (1898). (9) Hantzsch, Schnitter, *Ber.* 26, 2279-2282 (1887). (10) Mohlau, *Ber.* 19, 2010 (1886). (11) Carius, *Ann.* 143, 316 (1867). (12) Schuler, *Ann.* 69, 309-312 (1849). (13) Hunter, Kvalnes, *J. Am. Chem. Soc.* 54, 2574-2575, 2578 (1932). (14) Kvalnes, *J. Am. Chem. Soc.* 56,



667-670 (1934). (15) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; *Cent.* 1933, I 3133. (16) Herzberg, Hoppe (to A.G.F.A.) Ger. 368,171, Feb. 3, 1923; *Cent.* 1923, II 1187. (17) Den Hollander, *Rec. trav. chim.* 39, 482 (1920). (18) Morgan, Cooper, *J. Soc. Chem. Ind.* 43-T, 352-354 (1924). (19) Pfeiffer, Böttler, *Ber.* 51, 1828-1829 (1918). (20) Richter, *Ber.* 44, 3472 (1911).

(21) Staudinger, Bereza, *Ann.* 380, 261-262 (1911). (22) Ling, Baker, *J. Chem. Soc.* 63, 1319-1321 (1893). (23) Dodgson, *J. Chem. Soc.* 1930, 2498-2502. (24) Oliveri-Tortorici, *Gazz. chim. ital.* 27, II 585-586 (1897). (25) Levy, *Ber.* 18, 2367-2368 (1885). (26) Niemeyer, *Ann.* 228, 329-334 (1885). (27) Kehrmann, *Ber.* 21, 3319 (1888). (28) Nason, *J. Am. Chem. Soc.* 40, 1605 (1918).

## 3:4480 1-CHLOROANTHRAQUINONE



$C_{14}H_7O_2Cl$  Beil. VII - 787  
VII<sub>1</sub>-(409)

M.P. 164°	(1)	M.P. 161° cor.	(12)
162-163°	(2)	( <i>cont'd.</i> ) 161°	(13)
162.5° cor.	(3)	160.4-161.0°	(14)
162° cor.	(4) (5) (6)	160°	(15) (16)
162°	(7) (8) (9) (10) (11)	159.5°-160°	(17)
161-162° cor.	(3)	159°	(18)

[See also 2-chloroanthraquinone (3:4922).]

Yellow ndls. from  $C_6H_6$ , toluene, or alc.; eas. sol.  $C_6H_6$ , toluene, AcOH, nitrobenzene, or AmOH on htg.; spar. sol. alc. or lgr.

[For f.p./compn. data and diagram of system  $\bar{C}$  + 2-chloroanthraquinone (3:4922) (eutectic, m.p. 143.9-144.2°, contg. about 25%  $\bar{C}$ ) see (14).]

[For use in coloring oils, fats, and waxes see (19);  $\bar{C}$  is very widely used as intermed. in prepn. of many dyestuffs, but no general summary can be given here although selected examples occur in the following text.]

[For prepn. of  $\bar{C}$  from potassium salt of anthraquinonesulfonic acid-1 [Beil. XI-335, XI<sub>1</sub>-(81)] by htg with strong HCl + NaClO<sub>3</sub> (yields: 97-98% (3), 95% (4)) at 100° (3) (4) (10) (6) (8) (for use of this method in detn. of mixt. of anthraquinone- $\alpha$ - and  $\beta$ -sulfonic acids or their salts by f.p./compn. curve of resultant mixt. of  $\bar{C}$  + 2-chloroanthraquinone (3:4922) see (4)) or by actn of Cl<sub>2</sub> at 100° (20) see indic. refs.; from anthraquinonesulfonic acid-1 (0) or its Na salt (15) in dil. HCl on exposure to light see indic. refs.; from anthraquinonecarboxylic acid-1 with HCl + KClO<sub>3</sub> in s.t. at 200° for 12 hrs. see (22); from Na salt of anthracenesulfonic acid-1 [Beil. XI-194, XI<sub>1</sub>-(44)] with HCl + NaClO<sub>3</sub> at 100° see (21); from 1-chloroanthraquinonesulfonic acid-5 by electrolysis of alk. soln. see (23); from K salt of anthraquinonesulfonic acid-1 (see above) (24) or from anthraquinonesulfonyl chloride-1 (5) by btg. in s.t. with SOCl<sub>2</sub>, or from 1-anthraquinonylarsinic acid by 10 hrs. reflux with SOCl<sub>2</sub> (67), see indic. refs.]

[For prepn. of  $\bar{C}$  from 2-benzoyl-3- (or 6)-chlorobenzoic acid by ring closure with conc. H<sub>2</sub>SO<sub>4</sub> see (7) (25).]

[For prepn. of  $\bar{C}$  from 1-aminoanthraquinone (see below) via diazotization and use of Cu<sub>2</sub>Cl<sub>2</sub> reactn. see (26); from 1-nitroanthraquinone [Beil. VII-791, VII<sub>1</sub>-(415)] with Cl<sub>2</sub> in trichlorobenzene soln. at 160-165° see (27); from 1-hydroxyanthraquinone [Beil. VIII-338, VIII<sub>1</sub>-(650)] with PCl<sub>5</sub> in boilg. nitrobenzene see (28).]

[ $\bar{C}$  on htg. with conc.  $H_2SO_4$  at 200–205° for 9 hrs. reart. (29) to 2-chloroanthraquinone (3:4922).]

[ $\bar{C}$  on reductn. with Zn dust + conc. aq.  $NH_4OH$  under reflux yields (30) 1-chloroanthracene [Beil. VI-(324)], colorless lfts. from AcOH, m.p. 81–82° (2), 79° (30). —  $\bar{C}$  on reductn. with hydrazine hydrate in MeOH/KOH at 10 atm. and 135° for 1½ hrs. in pres. of Pd/CaCO<sub>3</sub> followed by access of air to the prod. gives (57% yield (31)) anthraquinone (14905). —  $\bar{C}$  on reductn. with Al powder + conc.  $H_2SO_4$  (32) (33) (3) (34) yields 1-chloroanthrone-9, yel. ndls. from  $CHCl_3$  + lt. pet., m.p. 115° (32), 114° (6);  $\bar{C}$  on reductn. with Sn + HCl in AcOH contg. PtCl<sub>4</sub>, however, gives the isomeric 4-chloroanthrone-9, yel. ndls. from  $CHCl_3$  + lt. pet., m.p. 118° (32) (note that although these two isomeric chloroanthrones have the same m.p. yet each depresses the m.p. of the other (32) and the earlier prod. of m.p. 106° (33) may have been a mixture). — For studies of oxidn.-reductn. potential of  $\bar{C}$  see (12) (17).]

[ $\bar{C}$  with MeOH/KOH at 80° yields (35) 1-methoxyanthraquinone [Beil. VII-37, VII-1-(651)], m.p. 169.5° —  $\bar{C}$  with 2-hydroxyanthraquinone + NaOAc + Cu powder in boilg. nitrobenzene gives (36) 1,2'-dianthraquinonyl ether [Beil. VIII-343], but m.p. is not reported. —  $\bar{C}$  with K xanthate + Cu powder boiled for 24 hrs. in AcOH or  $\bar{C}$  with alk. trithiocarbonate in boilg. nitrobenzene (41) gives (64% yield (37)) 2,3-bis(methoxynonyl) sulfide, red pr. from pyridine, m.p. 215° (37) (for disulfide see below). —  $\bar{C}$  with thiosalicylic acid (2-mercaptobenzoic acid) + solid KOH htd. in AcOH at 15° for 7 hrs. gives (66% yield (38)) S-(1-anthraquinonyl)thiosalicylic acid [Beil. X-10, 10-11] thls. from alc., m.p. 261° cor. (38); this prod. on htg. with  $PCl_5$  in nitrobenzene gives (98% yield (39)) 3,4-phthalylthioanthrone [Beil. XVII-(250)], or-red lfts., m.p. 340° cor. (39).]

[ $\bar{C}$  with NaOH + glycerol htd. at 120° is claimed (39) to yield anthraquinone (14905). —  $\bar{C}$  on htd. with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (42) yields 1-mercaptanthraquinone [Beil. XII-1, m.p. 187° (42)]; this prod. on oxidn. by air (43) readily yields 2,1'-dianthraquinonyl disulfide, m.p. 359° (45), also obt'd from  $\bar{C}$  with Na<sub>2</sub>S + S in boilg. alc. (46) (43) (47); from  $\bar{C}$  + K thiobenzoate in boilg. AcOH (50% yield (48)). —  $\bar{C}$  with  $H_2S_2O_8$  in alc. at 80° gives (17) 1-chloro-2-mercaptanthraquinone, or-red lfts. from AcOH, m.p. 220° in alc. (49) also di-(1-anthraquinonyl) disulfide.]

[ $\bar{C}$  with conc. aq.  $NH_4OH$  in pres. of Cu salts under press. at elevated temp. gives (50) (57) in alm. quant. yield 1-aminoanthraquinone [Beil. XIV-477, XIV-1-(651)], m.p. 212°. — Considerable analogies combinations of  $\bar{C}$  with various amines cannot be included here; however, note that  $\bar{C}$  with 1-aminoanthraquinone + NaOAc + CuCl<sub>2</sub> htd. in nitrobenzene yields (52) cf. (51) di-(1-anthraquinonyl) ether (for amplification of this topic see (54)). —  $\bar{C}$  with hydrazine hydrate + pyridine for 1½ hrs. gives (55% yield (56)) 1-hydrazinoanthraquinone [Beil. XI-(106)] cf. (57) lfts. from xylene, m.p. 225° cor. (54). — For reart. of  $\bar{C}$  with  $NH_4OH$  see (1).]

[For condens. of  $\bar{C}$  with 1-aminonaphthalene (53) or with 1-aminobenzene (54) as dyes for colorless azo dyes see indie. refs.; for condens. of  $\bar{C}$  with 1-aminobenzene in pres. of  $AlCl_3$  for prod. of triazoles see (55).]

[ $\bar{C}$  with Cu powder + 2,2'-bipyridine or in boilg. nitrobenzene yields (56) 2,2'-bis(methoxynonyl) disulfide, m.p. 215° (37) (for disulfide see below). —  $\bar{C}$  with 1-aminoanthraquinone + NaOAc + CuCl<sub>2</sub> htd. in nitrobenzene yields (52) cf. (51) di-(1-anthraquinonyl) ether (for amplification of this topic see (54)). —  $\bar{C}$  with 1-aminoanthraquinone + NaOAc + CuCl<sub>2</sub> htd. in nitrobenzene yields (52) cf. (51) di-(1-anthraquinonyl) ether (for amplification of this topic see (54)). —  $\bar{C}$  with 1-aminoanthraquinone + NaOAc + CuCl<sub>2</sub> htd. in nitrobenzene yields (52) cf. (51) di-(1-anthraquinonyl) ether (for amplification of this topic see (54)).]

185° (57), 180–182° (58); a mixt. of this prod. with corresp. prod. (m.p. 193°) from 2-chloroanthraquinone (3:4922) has m.p. 152–160° (58).]

[For formn. of addn. cpds. of  $\bar{C}$  with  $SbCl_5$  in  $CHCl_3$  see (16) (18); for formn. of 1-anthraquinonylpyridinium chloride from  $\bar{C}$  +  $AlCl_3$  in pyridine see (59).]

[ $\bar{C}$  on mononitration by soln. in 10 wt. pts. conc.  $H_2SO_4$  and addn. of  $HNO_3/H_2SO_4$  as directed (61) (62) gives (30% yield (61)) 1-chloro-4-nitroanthraquinone [Beil. VII-792, VII-415], cryst. from  $AcOH$ , m.p. 260–261° (63), 259° (61); note that 1-chloro-2-nitroanthraquinone (prepared by indirect means) has m.p. 257–258° (63). — For study of kinetics of nitration of  $\bar{C}$  see (64).]

[ $\bar{C}$  on monosulfonation, e.g., with fuming  $H_2SO_4$  (20%  $SO_3$ ) at 160° for 4 hrs. (65) (66), yields a mixt. of about equal parts of two monosulfonic acids eas. separable via their sodium salts; viz., 1-chloroanthraquinonesulfonic acid-6 (Na salt less sol. boilg. aq., corresp. sulfonyl chloride, pale yel. pr. from lgr., m.p. 207–208° dec.) and 1-chloroanthraquinonesulfonic acid-7 (Na salt more sol. boilg. aq., corresp. sulfonyl chloride, lemon-yel. pl. from  $C_6H_6$ , m.p. 200–201° dec.); the m.p. of mixts. of the two sulfonyl chlorides is depressed below 180° (65). —  $\bar{C}$  on sulfonation in the pres. of Hg salts but otherwise as above yields, however, a different result as the principal prod. is 1-chloroanthraquinonesulfonic acid-5 (corresp. sulfonyl chloride, yel. pl. from toluene, m.p. 243–244° dec. (65) (66)), accompanied by 1-chloroanthraquinonedisulfonic acid-4,5.

3:4480 (1) French, Achenbach, *Ber.* 43, 3255–3256 (1919). (2) Schilling, *Ber.* 46, 1066–1069 (1913). (3) Scott, Allen, *Org. Syntheses*, Coll. (4) Ullmann, Ochsner, *Ann.* 381, 2–6 (1911). Maki, *J. Soc. Chem. Ind. Japan*, Suppl. bindi Dougherty, Gleason, *J. Am. Chem. Soc.* 52, 11 *Chem.* 45, 19 (1932). (6) Eckert, *Ber.* 60, 16 (1927).

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(31) Busch, Weber, Zink, *J. prakt. Chem.* (2) 155, 107 (1940). (32) Barnett, Matthews, naschek, *Monatsh.* 39, 847 (1918). (31) *Ger.* 229,316, Dec. 13, 1910; *Cent.* 1911, *Int.* 1909, I 2104. (37) Perkin, Sewell, snecht, *Ber.* 44, 3126–3127 (1911); *Ger.* umura, Maeda, *J. Soc. Chem. Ind. Japan*, *C.A.* 32, 7447 (1938). (40) Bayer and 358.

(41) Bayer and Co., *Ger.* 204,772, Dec. 3, 1901; *Cent.* 1902, I 1342. (42) *Cent.* 1933, II 1764; *C.A.* 27, 1893 (1933); U.S.

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{61} Eckert, Steine  
137,782, Dec. 15, 190  
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C.A. 36, 4814-4815  
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23 (1938). {55} I.G., Brit.  
7, II 4394. {56} Ullmann,  
shire, *J. Chem. Soc.* 1927,  
{59} Mieg,  
Imperial Chem.  
and Co., Ger.  
5, 1922; *Cent.*  
35-342 (1911);  
9-1780 {66}  
{57} Steinkopf,

3:4485 2,3,5-TRICHLOROBENZOIC  
ACID



$C_7H_3O_2Cl_3$  Beil. IX - 345  
IX<sub>1</sub>—

M.P. 163° (1)  
162° (2) (3)

Ndis. from hot aq. (2). — Not volatile with steam. — Very spar. sol. cold aq. but sol. in org solv.

[For prepn. of  $\bar{C}$  from 2,3,5-trichlorotoluene (3:0010) by oxidn with 20%  $HNO_3$  in s.t. at 140° see (2); from 2,3,5-trichlorobenzaldehyde (3:1060) by oxidn. with  $KMnO_4$  see (3), for prepn. from corresp. nitrile by hydrolysis see (1).]

$\bar{C}$  on soln. in warm fuming  $HNO_3$  readily yields a mononitro cpd, 2,3,5-trichloro- $\alpha$ -nitrobenzoic acid, cryst. from alc, m.p. 158° (1).

$\bar{C}$  with excess  $PCl_5$  yields (1) 2,3,5-trichlorobenzoyl chloride, cryst. from EtOAc, m.p. 36° (1).

— Methyl 2,3,5-trichlorobenzoate: unrecorded.

— Ethyl 2,3,5-trichlorobenzoate: oil. (From  $\bar{C}$  + alc. +  $HCl$  (1).)

② 2,3,5-Trichlorobenzamide: from 2,3,5-trichlorobenzoyl chloride +  $(NH_4)_2CO_3$ ; ndis. from dil. AcOH, m.p. 204-205° (1).

— 2,3,5-Trichlorobenzanilide: unrecorded.

3:4485 (1) Matthews, *J. Chem. Soc.* 79, 43-49 (1901). (2) Cohen, Dakin, *J. Chem. Soc.* 81, 1331 (1902). (3) Hodgson, Beard, *J. Chem. Soc.* 1927, 2382.

3:4492 5-CHLORONAPHTHOQUINONE-1,4



$C_{10}H_6O_2Cl$  Beil. S.N. 674

M.P. 163° (1)

Yellow ndis. from alc or lgr. — Sublimes undecomposed. — Fairly eas. sol. AcOH or lgr.; moderately sol. alc.; spar. sol. aq.

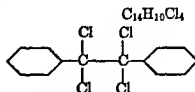
[For prepn. of  $\bar{C}$  from 5-chloro-1,4-diaminonaphthalene (5-chloronaphthylenediamine-1,2) by oxidn. of its hydrochloride with  $FeCl_3$  see (1).]

[ $\bar{C}$  with aniline (no details) gives (1) 2(37)-anilino-5-chloronaphthoquinone-1,4, red

bronzy ndls. from AcOH, m.p. 219° (1); note also that  $\bar{C}$  with aniline boiled for 1 hr. gives (1) a halogen-free cpd., dark violet cryst. from alc., m.p. 140°, but its structure has not been determined.]

3:4492 (1) Fries, Köhler, *Ber.* 57, 504-505 (1924).

3:4496 1,1,2,2-TETRACHLORO-1,2-DIPHENYLETHANE  
( $\alpha,\alpha,\alpha',\alpha'$ -Tetrachlorobibenzyl;  
tolane tetrachloride)



Beil. V - 601  
V<sub>1</sub>-(282)  
V<sub>2</sub>-(567)

M.P. 163° (1) (2) (3)  
162-163° (4)  
162° (5) (6)  
161-162° (7)  
161.5° (8)  
161° (9)

Colorless cryst. from AcOH, pct. ether,  $C_6H_6$ , or toluene. — Eas. sol. boilg.  $C_6H_6$ ; moderately sol. hot but spar. sol. cold pct. ether; spar. sol. alc. or ether.

$\bar{C}$  with *trans*-tolane dichloride (3:4210) forms an isomorphous mixt. (8) formerly erroneously regarded as an individual cpd. designated as "ditolano hexachloride."

## PREPARATION OF $\bar{C}$

### FROM DINUCLEAR INITIAL MATERIALS

[For prepn. of  $\bar{C}$  from benzil (1:9015) with excess  $PCl_5$  (32% yield (10)) in s.t. at 200° for 6-7 hrs. (5), or from *ms*-dichlorodesoxybenzoin ("chlorobenzil") [Beil. VII-436, VII<sub>1</sub>-(234)] with  $PCl_5$  in s.t. at 290° (11) in  $POCl_3$ ; refs.; from diphenylacetylene (tolane) [Beil. V-65]; or from either *cis*-(3:1380) or *trans*-(3:4210) refs.]

### FROM MONONUCLEAR INITIAL MATERIALS

From benzotrichloride. [For prepn. of  $\bar{C}$  from benzotrichloride (3:6540) by reduction in alc. with  $H_2$  + colloidal Pd (75% yield (4)) or  $H_2$  + Pd/ $BaCO_3$  (14) in alc.-alkali, or by htg. with Cu powder at 100° (6) or in  $C_6H_6$  under reflux for 4 hrs. (30-36% yield (5)) (1) cf. (10), see indic. refs.; for formn. of  $\bar{C}$  from benzotrichloride (3:6540) with excess dilute (0.2 N)  $MeMgCl$  in ether (7), with  $EtMgBr$  (3) or  $C_6H_5MgBr$  (3), or by pyrolysis over hot Pt (15), or by htg. with Ni in atm. of  $CO_2$  (16) see indic. refs.]

## CHEMICAL BEHAVIOR OF $\bar{C}$

[ $\bar{C}$  on reduction with conc.  $HI + P$  (1) or with  $H_2$  in alc.-alk. + Pd/ $CaCO_3$  (14) gives bibenzyl (1:7140), m.p. 52°.]

[ $\bar{C}$  on removal of two adjacent chlorine atoms with Fe powder in boilg. AcOH (12) cf. (5), with Cu powder at 160° (6), with excess conc. (2 N)  $MeMgCl$  in ether refluxed 4 hrs. (7), with  $H_2$  + hydrazine hydrate in  $MeOH/KOH$   $1\frac{1}{2}$  hrs. at b.p. (17), or with Zn dust in boilg. alc. (18) (5) (2) (10) gives either or both *trans*-(3:4210) and *cis*-(3:1380) tolane dichlorides; note that use of insufficient Zn gives (8) cf. (5) (10) the *cis*-tolane dichloride (3:1380) + an isomorphous mixt. of  $\bar{C}$  + *trans*-tolane dichloride (3:4210).]

[ $\bar{C}$  with Na/Hg in alc. gives (11) diphenylacetylene (tolane) (see ref. above), some stilbene (1:7250) and hibenzy (1:7149) also being formed (2).  $\bar{C}$  on htg. with Zn dust gives (2) stilbene (1:7250)]

[ $\bar{C}$  is very resistant to hydrolysis and is unattacked by  $H_2O$ , alc., or AcOH in s.t. at 207° (2); note, however, that  $\bar{C}$  with AcOH in s.t. at 230-250° or with  $H_2SO_4$  at 165° is claimed (2) to give benzil (1:9015).]

[ $\bar{C}$  is very resistant to action of boilg.  $HNO_3$  (2); note, however, that *p,p'*-dinitrotolane dichloride, m.p. 264-265° dec., has been prepd. indirectly (19) (from *p*-nitrobenzal(di)-chloride with acetone + KOH).]

[ $\bar{C}$  with anhydrous HF at 100° yields (20) 1,2-difluoro-1,2-diphenylethylene, m.p. 122-123° (20); however,  $\bar{C}$  with HF in pres. of  $HgO$  gives (20) 1,2-dichloro-1,2-difluoro-1,2-diphenylethane, m.p. 128-130° (20)]

3:4496 (1) Hanhart, *Ber.* 15, 901 (1882) (2) Liebermann, Homeyer, *Ber.* 12, 1971-1973 (1879). (3) Sanna, *Rev.*

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(1888) (6) C

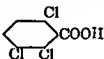
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# CHAPTER XI

## DIVISION A. SOLIDS

(3:4500-3:4999)

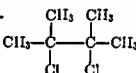
3:4500 2,3,6-TRICHLOROBENZOIC ACID   $C_7H_3O_2Cl_3$  Bell. IX - 345 IX<sub>1</sub>—

M.P. 163-164° (1)  
163-165° (2)

Cryst. from aq. (1).

[For prepn. of  $\bar{C}$  from 2,3,6-trichlorotoluene (3:0625) by oxidn. with  $HNO_3$  see (1) (2).]  
No further data on this compd. are recorded.

3:4500 (1) Cohen, Dakin, *J. Chem. Soc.* 81, 1332 (1902). (2) Feldman, Kopeliovitch, *Arch. Pharm.* 273, 491 (1935).

3:4520 2,3-DICHLORO-2,3-DIMETHYLBUTANE   $C_6H_{12}Cl_2$  Bell. I - 152 I<sub>1</sub>— I<sub>2</sub>—  
(Tetramethylethylene dichloride)

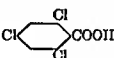
M.P. 164° (1)  
160° (2)  
159-160° (3)  
159° (4)

Colorless cryst. (from alc. (1)) with camphraceous odor. — Readily sublimes in open tubes on htg.; eas. sol. alc. ether.

[For prepn. of  $\bar{C}$  from tetramethylethylene glycol (pinacol) (1:5805) with fuming  $HCl$  (4) or with  $PCl_5$  (5) see (4) (5); for formn. from 2,3-dimethylbutane (di-isopropyl) (1:8515) with  $Cl_2$  in pres. of  $I_2$  see (4) (6).]

$\bar{C}$  with alc.  $KOH$  in s.t. at 130-140° gives (4) mainly 2,3-dimethylbutadiene-1,3 (1:8050), b.p. 68.7° (accompanied by unsatd. ethers, b.p. 136-146°) (4). [For study of behavior of  $\bar{C}$  with aq. alc.  $NaOH$  see (3).]

3:4520 (1) Kahovec, Wagner, *Z. physik. Chem.* B-47, 53 (1910). (2) Schorlemmer, *Ann.* 141, 186-187 (1867). (3) Tyshchenko, *J. Gen. Chem. (U.S.S.R.)* 6, 1380-1388 (1939); *C.A.* 34, 1611 (1910). (4) Kondakow, *J. prakt. Chem.* (2) 62, 169-174 (1900). (5) Couturier, *Ann. chim.* (6) 26, 443-441 (1892). (6) Silva, *Ber.* 6, 30 (1873).

3:4545 2,4,6-TRICHLOROBENZOIC ACID   $C_7H_3O_2Cl_3$  Bell. IX - 345 IX<sub>1</sub>—

M.P. 104° (1)  
102° (2)

M.P. (contd.) 160-161° (3)  
160° (4) (5)

Long ndls. from hot aq. (4); cryst. from  $C_6H_6$  + pct. eth. — Eas. sol. alc., ether, or  $CHCl_3$  (5).

[For prepn. of  $\bar{C}$  from 2,4,6-trichloroaniline (Beil. XII-627] via conversion by diazo reactn. to 2,4,6-trichlorobenzonitrile, m.p. 77.5° (1), 75° (6), thence to 2,4,6-trichlorobenzamide (see below) and hydrolysis of latter see (1) (4) (5) (2) (12); for prepn. of  $\bar{C}$  from 2,4,6-trichlorotoluene (3:0380) by oxidn. with  $HNO_3$  see (3).]

$\bar{C}$  on soln. in 5 pts conc.  $HNO_3$  yields (1) 2,4,6-trichloro-3-nitrobenzoic acid [Beil. IX-405], cryst. from  $CHCl_3$ , m.p. 169.2° (1)

$\bar{C}$  with  $PCl_5$  (5) (73% yield (2)) or with  $SOCl_2$  + pyridine (7) gives 2,4,6-trichlorobenzoyl chloride, b.p. 272° (5), 107-107.5° at 6 mm. (2), 120.1-120.4° at 3 mm (7). — This acid chloride is very stable to aq (5) and is alleged to give no ester with  $MeOH$  (5). [Note, however, that with  $EtOH$  reactn. is 99% complete in 1 min. (7).] [For study of reactn. of 2,4,6-trichlorobenzoyl chloride with  $MeMgCl$  (8) or  $MeMgBr$  (12) giving (50% yield (2)) di-(2,4,6-trichlorobenzoyl)methane, m.p. 160-161°, see (8), with  $MeMgBr$  giving 2,4,6-trichloroacetophenone, m.p. 51° (8) (14), see (8); with  $C_6H_6$  +  $AlCl_3$  yielding 2,4,6-trichlorobenzophenone, m.p. 103.5°, see (9)]

— Methyl 2,4,6-trichlorobenzoate: unrecorded. [ $\bar{C}$  +  $MeOH$  +  $HCl$  yields no ester (4) (10)]

— Ethyl 2,4,6-trichlorobenzoate: unrecorded. [ $\bar{C}$  +  $EtOH$  +  $HCl$  yields no ester (5)]

① 2,4,6-Trichlorobenzamide: m.p. 181° (1), 177° (6). [This amide has not been recorded as prepd. from the acid chloride +  $NH_3$ ; it has been obtd. only by partial hydrolysis (11) (6) (1) of 2,4,6-trichlorobenzonitrile (see above)] (The amide itself is only slowly hydrolyzed to  $\bar{C}$  by 75%  $H_2SO_4$  at 160° (6), but for conversion to  $\bar{C}$  via  $HNO_3$  see (11) (1) (2)]

② 2,4,6-Trichlorobenzanilide: from 2,4,6-trichlorobenzoyl chloride + aniline (12), ndls., m.p. 197° (12).

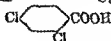
3:4545 (1) Montagne, *Rec. trav. chim.* 21, 383-388 (1902). (2) Fuson, Bertetti, Ross, *J. Am. Chem. Soc.* 54, 4351-4352 (1932). (3) Cohen, Dakin, *J. Chem. Soc.* 81, 1336 (1902). (4) Meyer, Sudborough, *Ber.* 27, 3151-3152 (1894). (5) Sudborough, *J. Chem. Soc.* 65, 1030 (1894). (6) Sudborough, Jackson, Lloyd, *J. Chem. Soc.* 71, 231-232 (1897). (7) Norris, Ware, *J. Am. Chem. Soc.* 61, 1415-1420 (1939). (8) Ross, Fuson, *J. Am. Chem. Soc.* 59, 1509-1510 (1937). (9) Montagne, *Rec. trav. chim.* 26, 279-280 (1907). (10) Meyer, *Ber.* 28, 1259 (1895).

(11) Sudborough, *J. Chem. Soc.* 67, 602 (1895). (12) Chapman, *J. Chem. Soc.* 1927, 1749. (13) Fuson, Van Campen, Wolf, *J. Am. Chem. Soc.* 60, 2269-2270 (1938). (14) Lock, Bäck, *Ber.* 70, 925 (1937).

### 3:4560 2,4-DICHLOROBENZOIC ACID

 $C_7H_4O_2Cl_2$ 

Beil. IX-342

 IX<sub>1</sub>-(141)


M.P. 164.3°	(1)
164°	(2) (3) (4)
163-164°	(5)
161.5-162.5°	(6)
161-162°	(20)

M.P. (contd.) 161°	(7)
159-160°	(8)
158°	(9)
156-158°	(10)

Cryst. from aq., alc. (3),  $C_6H_6$  or  $C_6H_5$  + 1gr. — Sublimes undecomposed in ndls. (9) or lfts. (10) — Eas. sol in boilg aq. or org solv. (10).

[For prepn. of  $\bar{C}$  from 2,4-dichlorotoluene (3:6290) by oxidn. with dil.  $HNO_3$  at 140° (9) (7) (3) or with  $KMnO_4$  (70% yield (1)) or by electrolytic oxidn. (65% yield (3)) see indic. refs.; from 2,4-dichlorobenzaldehyde (3:1800) via Cannizzaro reactn. see (5); from 2,4-dichloroaniline [Beil. VII-621] via conversion to and hydrolysis of 2,4-dichlorobenzoni-



trile see (4) (5); from 2,4-dichlorobenzotrithloride with 95%  $\text{H}_2\text{SO}_4$  see (5) (11) (12); for still other misc. methods see Beil. IX-342 + IX-1(141).]

$\bar{\text{C}}$  warmed at  $100^\circ$  with a mixt. of fuming  $\text{HNO}_3$  ( $D = 1.52$ ) + conc.  $\text{H}_2\text{SO}_4$  as directed (13) yields 2,4-dichloro-3,5-dinitrobenzoic acid, pr. from dilute alc., m.p.  $210-211^\circ$  (13), together with a trace of 2,4-dichloro-1,3-dinitrobenzene, m.p.  $103^\circ$ , insol. in  $\text{Na}_2\text{CO}_3$ . [A mononitrated  $\bar{\text{C}}$ , viz., 2,4-dichloro-5-nitrobenzoic acid, cryst. from 30%  $\text{AcOH}$ , m.p.  $161-163^\circ$  (11),  $162^\circ$  (18), and 2,4-dichloro-6-nitrobenzoic acid, cryst. from  $\text{C}_6\text{H}_6$ , m.p.  $189-190^\circ$  (19), have been prep'd. indirectly.]

$\bar{\text{C}}$  with  $\text{PCl}_5$  (14) or  $\text{SOCl}_2$  (15) (3) yields 2,4-dichlorobenzoyl chloride, b.p.  $150^\circ$  at 3-4 mm. (14),  $152-155^\circ$  at 30 mm. (16),  $91.9-92.5^\circ$  at 1 mm. (15). [For conv. of this acid chloride to 2,4,2',4'-tetrachlorodibenzoyl peroxide see (3).]

— Methyl 2,4-dichlorobenzoate: oil, b.p.  $132^\circ$  at 15 mm.,  $D_{20}^{20} = 1.572$  (21). [From  $\bar{\text{C}}$  by conv. to  $\text{Na}\bar{\text{A}}$  and htg. with  $\text{MeI}$  in  $\text{MeOH}$  for 20 hrs. (73% yield (21)).]

— Ethyl 2,4-dichlorobenzoate: constants unrecorded. [For study of rate of hydrolysis see (17).]

— 2,4-Dichlorobenzamide: unrecorded.

— 2,4-Dichlorobenzanilide: unrecorded.

3:4560 (1) Bornwater, Holleman, *Rec. trav. chim.* 31, 226-230 (1912). (2) Lock, Böck, *Ber.* 70, 923 (1937). (3) Fichter, Adler, *Helv. Chim. Acta* 9, 286-287 (1926). (4) Gomberg, Cone, *Ann.* 370, 183 (1909). (5) van der Lande, *Rec. trav. chim.* 51, 103 (1932). (6) Gasmann, Hartmann, *J. Am. Chem. Soc.* 63, 2394 (1941). (7) Wynne, *J. Chem. Soc.* 1936, 703. (8) Cohen, Dakin, *J. Chem. Soc.* 79, 1129 (1901). (9) Lellmann, Klotz, *Ann.* 231, 315-316 (1855). (10) Krauss, *Ber.* 37, 221 (1904).

(11) Villiger, *Ber.* 61, 2598 (1928). (12) Ger. 234,290, May 4, 1911; *Cent.* 1911, I 1567. (13) Borache, Bahr, *Ann.* 402, 90-91 (1914). (14) Cohen, Briggs, *J. Chem. Soc.* 83, 1213-1214 (1903). (15) Norris, Ware, *J. Am. Chem. Soc.* 61, 1418 (1939). (16) B.A.S.F. Ger. 231,690, Jan. 10, 1921 [*C.A.* 15, 2102 (1921)]. (17) Blakey, McCombie, Sudborough, *J. Chem. Soc.* 1926, 2563-2568. (18) Grimm, Günther, Tittus, *Z. physik. Chem. B-14*, 184 (1931). (19) Ruggli, Zaeslin, *Helv. Chim. Acta* 19, 439 (1936). (20) Roberts, Turner, *J. Chem. Soc.* 1927, 1846. (21) Samant, *Ber.* 75, 1011 (1942).

### 3:4580 3,5-DICHLOROPHTHALIC ACID


 $\text{C}_6\text{H}_4\text{O}_4\text{Cl}_2$ 

Beil. IX - 817  
IX<sub>1</sub>—

M.P.  $164^\circ$  (1)  
 $164^\circ$  dec. (2)

[See also 3,5-dichlorophthalic anhydride (3:2375).]

Colorless ndls. or thls. from aq.  $\text{HCl}$ ; readily sol. in cold alc., ether, or acetone, but spar. sol. in  $\text{C}_6\text{H}_6$  or  $\text{CHCl}_3$  even on boil.

[For prep'n. of  $\bar{\text{C}}$  from 3,5-dichlorophthalic anhydride (3:2375) on boil. with aq. see (1) (2); from aq. soln. of  $\text{NH}_4\bar{\text{H}}\bar{\text{A}}$  by passing in  $\text{HCl}$  gas see (1) (2); from 3,5-dichloro-1,2-dimethylbenzene [Beil. V-364] (itself obtd. in good yield from dimethyldihydroresorcinol ("methone") (1:0768) with  $\text{PCl}_5$  in  $\text{CHCl}_3$  (2) (3)) by oxidn. with dil.  $\text{HNO}_3$  in s.t. at  $190-200^\circ$  see (2).]

Salts.  $\text{NH}_4\bar{\text{H}}\bar{\text{A}}$ , spar. sol. aq., eas. prep'd. by mixing aq. solns. of  $(\text{NH}_4)_2\bar{\text{A}}$  +  $\bar{\text{C}}$ ;  $\text{Ag}\bar{\text{A}}$ , white curdy ppt. from warm aq. soln. of  $(\text{NH}_4)_2\bar{\text{A}}$  by addn. of aq.  $\text{AgNO}_3$ .

Esters. Dimethyl 3-chlorophthalate and methyl hydrogen 3-chlorophthalate are unreported: diethyl 3-chlorophthalate (from  $\text{Ag}\bar{\text{A}}$  with  $\text{EtI}$  in dry ether) is oil, b.p.  $312-313^\circ$  at 760 mm. (2); ethyl hydrogen phthalate is unreported.

$\bar{C}$  on htg. alone (1) or with  $\text{AcCl}$  (2) yields 3,5-dichlorophthalic anhydride (3:2375), m.p.  $89^\circ$ .

3:4580 (1) Waldmann, Schwenk, *Ann* 487, 293 (1931). (2) Crossley, LeSueur, *J. Chem. Soc.* 81, 1536-1537 (1902). (3) Crossley, LeSueur, *J. Chem. Soc.* 82, 826-827 (1902).

3:4600 2,6-DICHLOROHYDROQUINONE  
(*m*-Dichlorohydroquinone)



$\text{C}_6\text{H}_4\text{O}_2\text{Cl}_2$

Beil. VI - 850  
VI<sub>1</sub>-(417)

M.P. $165^\circ$	(1)
$164^\circ$	(2)
$163-164^\circ$	(3)
$163^\circ$	(4)
$161-162^\circ$ cor.	(7)
$161^\circ$	(5)
$157-158^\circ$	(6)

[See also 2,6-dichlorobenzoquinone-1,4 (3:3750).]

Colorless lfts from dil. alc.; ndls. from aq. or  $\text{C}_6\text{H}_6$ . — Sublimes

[For prepn. of  $\bar{C}$  from 2,6-dichlorobenzoquinone-1,4 (3:3750) by reductn. with  $\text{SO}_2$  in aq. see (80% yield (5)) (6) (7) (note, however, that the quinone in dil. aq.  $\text{NaOH}$  under  $\text{N}_2$  with  $\text{SO}_2$  is in part reduced to  $\bar{C}$  and in part sulfonated to mono- and disulfonic acids (8)); from 2,4,6-trichlorophenol (3:1673) in 2 *N*  $\text{H}_2\text{SO}_4$  on electrolytic oxidn. see (4); from 3,5-dichloro-4-hydroxybenzaldehyde (3:4400) in *N*  $\text{KOH}$  with  $\text{H}_2\text{O}_2$  see (3); from sodium benzoquinone-1,4-sulfonate with conc.  $\text{HCl}$  above  $20^\circ$  in  $\text{CO}_2$  (below  $20^\circ$  chlorohydroquinonesulfonic acid results) see (1) (9).]

[For use of  $\bar{C}$  as antioxidant and gum inhibitor in cracked gasoline see (10); for use in aq. petroleum emulsion as insecticidal oil spray see (11); for use as vulcanization accelerator see (18).]

$\bar{C}$  on oxidn. with  $\text{CrO}_3$  (12) or with excess aq.  $\text{FeCl}_3$  on warming (3) yields 2,6-dichlorobenzoquinone-1,4 (3:3750) (the intermediate quinhydrone epd., brown powder or pr. or dark ndls. (5), m.p.  $135^\circ$  (13), may separate with insufficient oxidant). [For studies on oxidn.-reductn. potential of system:  $\bar{C}$  + 2,6-dichlorobenzoquinone-1,4 (3:3750) see under latter.]

[ $\bar{C}$  in conc.  $\text{H}_2\text{SO}_4$  with chloral hydrate (3:1270) (2 moles) gives (64% yield (14)) 5,7-dichloro-6-hydroxy-2,4-bis-(trichloromethyl)benzodioxin-1,3, colorless pl. from boilg. alc.,  $\text{CHCl}_3$ ,  $\text{C}_6\text{H}_6$ , or pet. eth., m.p.  $114-115^\circ$  (14).]

— 2,6-Dichlorohydroquinone diacetate: ndls. and pr. from aq. alc., m.p.  $98^\circ$  (2).  $85-86^\circ$  on rap. htg.,  $111-113^\circ$  on slow htg. (15),  $75.5^\circ$  (7),  $66.5^\circ$  (16). (The reasons for these divergences appear never to have been explained.) [From  $\bar{C}$  with  $\text{Ac}_2\text{O}$  (16) (15).]

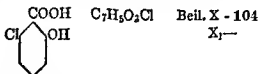
① 2,6-Dichlorohydroquinone dibenzoate: colorless ndls. from alc., m.p.  $105^\circ$  (16). [From  $\bar{C}$  on htg. with  $\text{BaCl}$  (16).]

② 2,6-Dichlorohydroquinone dimethyl ether: m.p. not reported. [From  $\bar{C}$  in dil. aq. alk. with  $\text{Me}_2\text{SO}$ , (17); this prod. with 3-4 pts. cold fumg.  $\text{HNO}_3$  nitrates yielding (17) 2,6-dichloro-3,5-dinitrohydroquinone dimethyl ether, colorless cryst. from alc., m.p.  $121-123^\circ$  (17).]

3:4600 (1) Seyewetz, *Compt. rend.* 156, 902 (1913). (2) Kehrman, Tiesler, *J. prakt. Chem.* (2)-40, 481 (1889). (3) Dakin, *Am. Chem. J.* 42, 491 (1909). (4) Fichter, Stocker, *Ber.* 47, 2916 (1914). (5) Conant, Fieser, *J. Am. Chem. Soc.* 45, 2202-2204 (1923). (6) Faust, *Ann.* 149, 155 (1869). (7) van Erp, *Ber.* 58, 965 (1925). (8) Dodgson, *J. Chem. Soc.* 1930, 2498-2502 (9) Seyewetz, Paris, *Bull. soc. chim.* (4) 13, 489-490 (1913). (10) Clarke, Towne (to Texas Co.), U.S. 2,923,871, Dec. 19, 1935; *Cent.* 1036, I 2671; *C.A.* 30, 951 (1936).

(11) Yates (to Shell Development Co.), U.S. 1,778,240, Oct. 14, 1930; *Cent.* 1031, I 2799; *C.A.* 24, 5928 (1930). (12) Den Hollander, *Rec. trav. chim.* 39, 481-482 (1920). (13) Ling, Baker, *J. Chem. Soc.* 63, 1321-1322 (1893). (14) Chattaway, Calvet, *J. Chem. Soc.* 1928, 2915, 2918. (15) Ling, *J. Chem. Soc.* 61, 560 (1892). (16) Levy, *Ber.* 16, 1445-1446 (1883). (17) Kohn, Marberger, *Monatsh.* 45, 654-656 (1924). (18) Fisher (to Naugatuck Chem. Co.), French 749,078, Feb. 3, 1933, *Cent.* 1033, I 3134.

3:4610 6-CHLORO-2-HYDROXYBENZOIC  
ACID  
(6-Chlorosalicylic acid)



M.P. 166° (1)

Colorless ndls. from aq., grad. turning red in air. — Sol. in aq. and most org. solvents; not volatile with steam.

[For prepa. of  $\bar{\text{C}}$  from 6-chloro-2-aminobenzoic acid (6-chloroanthranilic acid) [Beil. XIV-366, XIV<sub>1</sub>-(548)] by diazotization and boilg. with aq. (*m*-chlorophenol (3:0255) is also formed) see (1).]

$\bar{\text{C}}$  with  $\text{FeCl}_3$  soln. gives violet color.

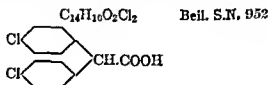
For  $\text{NH}_4\bar{\text{A}}$ ,  $\text{K}\bar{\text{A}}$ ,  $\text{Ba}\bar{\text{A}}$ ,  $\text{Ag}\bar{\text{A}}$ , all sol. in aq., see (1).

[The methyl ether of  $\bar{\text{C}}$ , viz., 6-chloro-2-methoxybenzoic acid, m.p. 141° (2), has been obtd. indirectly from 2-chloro-6-methoxytoluene [Beil. VI-359] by  $\text{KMnO}_4$  oxidn. (2).]

[For esterification of  $\bar{\text{C}}$  with glycol monoethers and use of prods. as plasticizers see (3).]

3:4619 (1) Cohn, *Mitt. Technol. Gewerb.-Mus. Wien* 11, 178-182; *Cent.* 1901, II 925. (2) Ullmann, Panchaud, *Ann.* 350, 113 (1906). (3) Grether, DuVall (to Dow Chem. Co.), U.S. 2,234,374 March 11, 1941; *C.A.* 35, 3738 (1941).

3:4612 DI-(*p*-CHLOROPHENYL)ACETIC  
ACID



M.P. 166.0-166.5° u.c. (1)  
163-164° (2)

Colorless cryst. from dil. alc. Neut. Eq. = 281.

[For prepn. of  $\bar{\text{C}}$  from 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane ("DDT") (3:3298) by action of excess  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  in ethylene glycol under reflux for 10-12 hrs. (33% yield) see (1); from 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (3:2438) by similar treatment (1) or with alc. KOH in a.t. at 150-160° for 24 hrs. (57% yield (2)) see<sup>5</sup>indie. refs.; for prepn. of  $\bar{\text{C}}$  from chlorobenzene (3:7903) by condensation with glyoxylic acid monohydrate  $(\text{HO})_2\text{CH.COOH}$  in pres. of conc. + fuming  $\text{H}_2\text{SO}_4$  at 20° (18.6% yield) see (1).]

$\bar{\text{C}}$  with KOH in ethylene glycol refluxed 10-12 hrs. loses  $\text{CO}_2$  giving alm. 100% yields (1) of 4,4'-dichlorodiphenylmethane (3:1057), m.p. 55°.

Note that  $\bar{\text{C}}$  is one of the metabolic prods. obtd. from the urine after administration of "DDT" (3:3298) to rabbits.

3:4612 (1) White, Sweeney, *U S. Pub. Health Repts.* 60, 66-71 (1945). (2) Grummitt, Buck, Jenkins, *J. Am. Chem. Soc.* 67, 156 (1945).

3:4615 6-CHLORO-3-METHYLBENZOIC ACID



$C_8H_7O_2Cl$  Beil. IX - 479  
IX<sub>1</sub>—

M.P. 167° u.c. (1) (2)  
163-166° (3)

Colorless ndls. from aq. or alc.

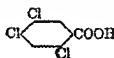
[For prepn. of  $\bar{C}$  from 6-chloro-3-methylacetophenone [Beil. VII-307] by oxidn. with  $KMnO_4$  or dil.  $HNO_3$  see (1); from  $\beta$ -chloroethyl 6-chloro-3-methylphenyl ketone (2) by oxidn. at 100° with mixt. of equal pts. conc.  $HNO_3$  ( $D = 1.42$ ) and water see (2); from *p*-chlorotoluene (3:8287) in  $CS_2$  with oxalyl (di)chloride (3:5060) +  $AlCl_3$  for 20 hrs. at room temp. see (3)]

[ $\bar{C}$  with 6 pts.  $SOCl_2$  gives (alm. quant. yield (3)) 6-chloro-3-methylbenzoyl chloride, b.p. 165-167° at 85 mm. (3).]

$\bar{C}$  on oxidn. with  $KMnO_4$  yields (1) (3) 4-chlorobenzenedicarboxylic acid-1,3 (4-chloroisophthalic acid) (3:4980), m.p. 286° u.c. (1).

3:4615 (1) Claus, *J. prakt. Chem.* (2) 46, 27 (1892) (2) Mayer, Müller, *Ber.* 60, 2281 (1927). (3) Scholl, Meyer, Keller, *Ann.* 513, 298 (1934).

3:4630 2,4,5-TRICHLOROBENZOIC ACID



$C_7H_2O_2Cl_3$  Beil. IX - 345  
IX<sub>1</sub>-(141)

M.P. 168° (1)  
164-165° (2)  
163° (3)  
162-164° (4)  
160-163° (6)

Ndls. from aq. or dil. alc. — Alm. insol. cold aq., eas. sol. cold abs. alc. (4). — Sublimes in ndls. (4).

[For prepn. of  $\bar{C}$  from 1,2,4-trichlorobenzene (3:6420) via nitration, reduction, conversion via diazo reactn. to 2,4,5-trichlorobenzonitrile, m.p. 104° (1), and subsequent indirect hydrolysis see (1); from 2,4,5-trichlorotoluene (3:2100) by oxidn. with  $HNO_3$  (4) (6) or  $CrO_2$  (5) see (4) (5) (6); from 2,4,5-benzotrichloride via htg. with aq. in a.t. at 260° see (3); from 3,4-dichlorobenzoic acid (3:4925) +  $Ca(OCl)_2$  see (3); from  $HNO_3$  oxidn. of certain fractions of chlorinated isopropylbenzene (cumene) see (2)]

For salts, viz.,  $NH_4\bar{A}$ ,  $Ca\bar{A}_2 \cdot 2H_2O$ ;  $Sr\bar{A}_2 \cdot 4H_2O$ ;  $Ba\bar{A}_2 \cdot 7H_2O$ , see (3).

$\bar{C}$  on nitration with hot mixt. of equal vols. conc.  $HNO_3$  + conc.  $H_2SO_4$  yields (3) 2,4,5-trichloro-*z*-nitrobenzoic acid, ndls. from aq., m.p. 220° (3).

$\bar{C}$  with  $PCl_5$  (3) or  $SOCl_2$  (1) yields 2,4,5-trichlorobenzoyl chloride, b.p. 272° sl. dec. (3), 125° at 2 mm. (1); m.p. abt. 28° (1), 41° (3).

— Methyl 2,4,5-trichlorobenzoate: unrecorded.

— Ethyl 2,4,5-trichlorobenzoate: from  $\bar{C}$  +  $EtOH$  +  $HCl$  (3); m.p. 65° (1) (3).

⊕ 2,4,5-Trichlorobenzamide: from 2,4,5-trichlorobenzoyl chloride + cold conc.  $NH_4OH$  (3), ndls. from  $C_6H_6$ , m.p. 167.5° (3), 168° (1). [For conversion of this amide to  $\bar{C}$  via  $HNO_2$  see (1).]

3:4630 (1) Baker, Tweed, *J. Chem. Soc.* 1911, 800. *et Phys.* 8, No (3) Beilstein, 1. (1902). (5) J 273, 494 (1935).

3:4650 2,3-DICHLOROBENZOIC ACID



$C_7H_4O_2Cl_2$  Beil. IX-342 IX<sub>1</sub>—

M.P. 168.3° cor. (1)  
166° (2)  
164° (3)  
163° (4)

Cryst. from  $C_6H_6$  or from 30% AcOH (1).

[For prepn. of  $\bar{C}$  from 2,3-dichlorotoluene (3:6345) with alk.  $KMnO_4$  (1) (2) or with dil.  $HNO_3$  in s.t. at 140° (2) (4) see (1) (2) (4); from benzoic acid (1:0715) by chlorination with  $KClO_3 + HCl$  (3) (6) or with  $Ca(OCl)_2$  (7) see (5) (6) (7).]

For f.p./compn. data on mixts. of  $\bar{C}$  with 2,5-dichlorobenzoic acid (3:4340), m.p. 154.4°, see (1).

$\bar{C}$  on htg. with limo yields (6) o-dichlorobenzene (3:6055).

$\bar{C}$  is unaffected by conc.  $H_2SO_4$  at 300° (6) and scarcely affected by htg. with fuming  $HNO_3$  (10). — However,  $\bar{C}$  dislvd. in boulg. non-fuming  $HNO_3$  and treated as directed (10) with conc.  $H_2SO_4$  yields 2,3-dichloro-x-nitrobenzoic acid, m.p. 214–215° u.c. (10).

$\bar{C}$  with  $PCl_5$  yields (8) 2,3-dichlorobenzoyl chloride, b.p. 140° at 14 mm. (8). [This acid chloride is formed during chlorination of benzoyl chloride in presence of  $FeCl_3$  where it constitutes 23% of the dichlorinated fraction (8).]

— Methyl 2,3-dichlorobenzoate: unrecorded.

— Ethyl 2,3-dichlorobenzoate: m.p. unrecorded. [For study of velocity of hydrolysis see (9).]

— 2,3-Dichlorobenzamide: unrecorded.

— 2,3-Dichlorobenzanilide: unrecorded.

7, 162 (1887).  
*Chem. Soc.* 79,  
-1627 (1887).  
(9) Blakey,  
*Ber.* 20, 1624

(1887).

3:4670 5-CHLORO-2-METHYLBENZOIC ACID



$C_8H_7O_2Cl$  Beil. S.N. 941

M.P. 168.5–169.5° (1)  
168° (2)

Colorless ndls. from alc.

Note that the materials of m.p. 130° (3) and 137° (4) formerly supposed to have been  $\bar{C}$  were believed (1) to have been mixtures of  $\bar{C}$  with the isomeric 4-chloro-2-methylbenzoic acid (3:4700).  
5-chloro-2-methylaniline [Beil. XII-835, XII<sub>1</sub>-(384)] via conv. nitrile (1) (2), ndls. from pet. ether, m.p. 48° (2), 45–46° (1), and with 70%  $H_2SO_4$  (2) see indic. refs.]

$\bar{C}$  yields (no details) an acid chloride which with  $C_6H_6 + AlCl_3$  in  $CS_2$  gives (2) 5-chloro-2-methylbenzophenone, m.p.  $41^\circ$  (2), b.p.  $191^\circ$  at 12 mm. (2).]

$\bar{C}$  on oxidn. with  $KMnO_4$  yields (1) 4-chlorophthalic acid (3:4390), m.p.  $151^\circ$  (1).

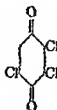
— Methyl 5-chloro-2-methylbenzoate: unreported.

— Ethyl 5-chloro-2-methylbenzoate: b.p. unreported,  $D_4^{20} = 1.1628$  (1),  $n_{D_4}^{20} = 1.52483$  (1).

— 5-Chloro-2-methyl benzamide: unreported.

3:4670 (1) von Auwers, Harres, *Z. physik. Chem.* A-143, 16-18 (1929). (2) de Diesbach, Döbbelmann, *Helv. Chim. Acta* 14, 375 (1931). (3) Claus, Bayer, *Ann.* 274, 308-309 (1893). (4) Claus, Stapelberg, *Ann.* 274, 311 (1893).

### 3:4672 2,3,5-TRICHLORO-BENZO- QUINONE-1,4



$C_6HO_2Cl_3$

Bell. VII - 634  
VII<sub>1</sub>-(347)

M.P. 169-170°	(1)
168° cor.	(2)
165-166°	(3) (10) (17)
165°	(4)
164-166°	(5)
163-164°	(22)
163°	(30)
162-163°	(6) (7)

Yellow lfts. from alcohol; reddish yel. lfts. from  $CHCl_3$ /gr. — Insol. cold aq.; spar. sol. cold alc.; eas. sol. hot alc. or ether. —  $\bar{C}$  is sublimable [for study of sublimation press see (8)]

[For studies of heat of formation see (9); for studies of heat of combustion see (10) (11).]

[For studies of bactericidal actn. of  $\bar{C}$  see (12); for patent on use of  $\bar{C}$  as vulcanization accelerator see (13)]

### PREPARATION OF $\bar{C}$

From 2,3,5-trichlorohydroquinone. [For prepn. of  $\bar{C}$  from 2,3,4-trichlorohydroquinone (3:4052) by oxidn., e.g., with  $CrO_3$  at  $6^\circ$  (10), conc.  $HNO_3$  (14) (5) see indic. refs.]

From phenol or chlorinated phenols. [For prepn. of  $\bar{C}$  from pheool (1:1420) via sulfonation followed by oxidn. with  $KClO_3 + HCl$  see (3) (15) cf. (22), note that by this method both  $\bar{C}$  and 2,3,5,6-tetrachlorobenzoquinone-1,4 ("chloranil") (3:4978) are produced; for sepn. of  $\bar{C}$  from latter see (5) (16).]

[For prepn. of  $\bar{C}$  from 2,3,5-trichlorophenol (3:1340) or from 2,3,6-trichlorophenol (3:1160) with fuming  $HNO_3$  on protracted htg. (17), or from 2,4,6-trichlorophenol (3:1673) with mixt. of conc.  $HNO_3 +$  conc.  $HCl$  boiled for a few minutes (2), or from 2,3,4,6-tetrachlorophenol (3:1687) by oxidn. with 5 wt. pts. fuming  $HNO_3$  (70% yield (1)), see indic. refs.]

From amines, aminophenols, etc. [For formn. of  $\bar{C}$  from aniline during electrolytic oxidn. in  $HCl$  soln. see (18); from *p*-aminophenol hydrochloride with  $Ca(OCl)_2$  soln. see (10); from 2,3,5-trichloro-4-aminophenol hydrochloride by action of  $Br_2$  (20) or  $NaOBr$

{30}; from benzal *p*-anisidine or benzal *p*-phenetidine by treatment with *ter*-AmOCl (3:9287) followed by subsequent oxidn. with  $K_2Cr_2O_7/H_2SO_4$  see {4}.]

From various derivs. of  $\bar{C}$  by hydrolysis. [For formn. of  $\bar{C}$  from various imide derivs. of  $\bar{C}$  by acid hydrolysis, e.g., from the corresp. *N*-(*p*-chlorophenyl)imide [Beil. XII-611] {21}, *N*-(2,4,6-trichlorophenyl)imide [Beil. XII-628] {22} {7}, or *N*-(2,4-dinitrophenyl)imide [Beil. XII-754] {23}, see inde. refs.]

From miscellaneous sources. [For formn. of  $\bar{C}$  from  $C_6H_6$  (1:7400) by oxidn. with  $CrO_2Cl_2/AcOH$  {24}, from copper salt of quinic acid [Beil. X-535, XI-(270)] by oxidn. with  $MnO_2/NaCl/H_2SO_4$  {14}, or from benzoquinone-1,4 (1:9025) with  $Cl_2$  {25} see inde. refs.]

### CHEMICAL BEHAVIOR OF $\bar{C}$

Reduction.  $\bar{C}$  with aq.  $SO_2$  {5} {14} {15} {16}, or  $\bar{C}$  in ether soln. with aq.  $SO_2$  {1} reduces to 2,3,5-trichlorohydroquinone (3:4052). [Note that this reaction is used {16} to separate  $\bar{C}$  from 2,3,5,6-tetrachlorobenzoquinone-1,4 ("chloranil") (3:4978) since the latter is but slowly reduced by aq.  $SO_2$ .] [For studies of oxidn.-reduction potential of system  $\bar{C}$  + 2,3,5-trichlorohydroquinone (3:4052) see {6} {26} {27}.]

Oxidation.  $\bar{C}$  with strong  $HNO_3$  on digestion is degraded with formn. of trichloronitromethane ("chloropicrin") +  $CO_2$  {15}.

Chlorination. [ $\bar{C}$  with  $Cl_2$  reacts only very slowly; however,  $\bar{C}$  with  $Cl_2 + I_2 + aq.$  {15}, or  $\bar{C}$  with  $Cl_2 + HCl$  {28}, gives 2,3,5,6-tetrachlorobenzoquinone-1,4 ("chloranil") (3:4978).]

Reaction with  $HCl$ .  $\bar{C}$  with conc.  $HCl$  on protracted boilg. {29} {3}, or  $\bar{C}$  with fuming  $HCl$  in s.t. at  $130^\circ$  {30}, gives 2,3,5,6-tetrachlorohydroquinone (3:4941).

Behavior of  $\bar{C}$  with other inorganic reactants. With aq. alkali. [ $\bar{C}$  with dil. aq.  $KOH$  turns green and then dis. to a red-brown soln. from which upon acidification is pptd. {5} 2,5-dichloro-3,6-dihydroxybenzoquinone-1,4 ("chloroanilic acid") (3:4970).]

With aq.  $K_2SO_3$ . [ $\bar{C}$  dis. in warm aq.  $K_2SO_3$  or  $KHSO_3$  and on cooling ppts. {31} the potassium salt of 2,3,5-trichlorohydroquinonesulfonic acid-6 [Beil. XI-300]; the mother liquor conts. a cpd. which on boilg. with  $KOH$  gives {31} the salt of 2,5-dihydroxybenzoquinone-1,4-disulfonic acid-3,6 [Beil. XI-353].]

With  $NH_3$ . [ $\bar{C}$  with alc.  $NH_3$  reacts vigorously yielding {3} a dark soln. from which can be obt'd. in small amt. 3,6-dichloro-2,5-diaminobenzoquinone-1,4 ("chloranilamide") [Beil. XIV-144].]

With  $PCl_5$ . [ $\bar{C}$  with  $PCl_5 + POCl_3$  in s.t. at  $180-200^\circ$  gives {5} hexachlorobenzene (3:4949).]

Behavior of  $\bar{C}$  with organic reactants. With phenol.  $\bar{C}$  with  $K$  phenolate (2 moles) at  $100^\circ$  for 20 min. gives {32} 3-chloro-2,5-diphenoxybenzoquinone-1,4, or, tbs. from alc., m.p.  $169-170^\circ$  {32}.

With 2,3,5-trichlorohydroquinone.  $\bar{C}$  (1 mole) with 2,3,5-trichlorohydroquinone (1 mole) (3:4052) in  $CHCl_3$  soln. gives on evapn. {6} {33} the corresp. quinhedrone, green-black cryst., m.p.  $114-115^\circ$  {6},  $103^\circ$  {33}.

With acetyl chloride.  $\bar{C}$  with  $AcCl$  in s.t. at  $160-180^\circ$  gives {5} 2,3,5,6-tetrachlorohydroquinone diacetate (cf. 3:4941).

With aniline. [ $\bar{C}$  (1 mole) with aniline hydrochloride (1 mole) in  $AcOH$  on boilg. and subsequent partial evapn. {34} cf. {35} gives (66.5% yield {34}) 2,3,5-trichloro-6-anilino-benzoquinone-1,4 [Beil. XIV-137], blue lfts. from hot alc., but without def. m.p. {35}.— $\bar{C}$  with aniline (excess) in alc. {30} {35} or  $AcOH$  {35} gives, however, 2,5-dichloro-3,6-dianilinobenzoquinone-1,4 [Beil. XIV-144, XIV<sub>1</sub>-(421)], yel.-brown metallic lfts. from  $C_6H_6$ , m.p.  $290^\circ$  {35},  $285-290^\circ$  {30}.]

With triphenylphosphine.  $\bar{C}$  with 20% soln. of  $(C_6H_5)_3P$  in  $CHCl_3$  gives (36) wine-red color; note, however, that a very similar behavior is shown by 2,3,5,6-tetrachlorobenzoquinone-1,4 ("chloranil").

3:4672 (1) Biltz, Giese, *Ber.* 37, 4016-4017 (1904). (2) Leger, *Bull. soc. chim.* (4) 3, 581-582 (1908). (3) Knapp, Schultz, *Ann.* 210, 174-176, 180-181 (1881). (4) Musante, Fusco, *Gazz. chim. ital.* 66, 647-648 (1936). (5) Graebe, *Ann.* 146, 22-30 (1868). (6) Conant, Fieser, *J. Am. Chem. Soc.* 45, 2206-2207 (1923). (7) Bradfield, Cooper, Orton, *J. Chem. Soc.* 1927, 2858-2859. (8) A. S. Coolidge, M. S. Coolidge, *J. Am. Chem. Soc.* 49, 101-104 (1927). (9) Sjöström, *Svensk Kem. Tid.* 48, 121-124 (1936), *Cent.* 1937, I 58, *C.A.* 30, 6634 (1936). (10) Valeur, *Ann. chim.* (7) 21, 496-497 (1900).

(11) Swietoslawski, Stanczewska, *J. chim. phys.* 22, 399-401 (1925). (12) Morgan, Cooper, *J. Soc. Chem. Ind.* 43-T, 352-354 (1924). (13) Fisher (to Naugatuck Chem. Co.) French 740,978, Feb. 3, 1933, *Cent.* 1933 I 3134, *C.A.* 27, 2845 (1933). (14) Stadeler, *Ann.* 69, 301, 322 (1849). (15) Stenhouse, *Ann., Suppl.* 6, 209-212, 216-219 (1868). (16) Graebe, *Ann.* 263, 28-30 (1891). (17) Lampert, *J. prakt. Chem.* (2) 33, 382-383 (1886). (18) Erdelyi, *Ber.* 63, 1201-1202 (1930). (19) Schmitt, Andresen, *J. prakt. Chem.* (2) 23, 436-437 (1881). (20) Schmitt, Andresen, *J. prakt. Chem.* (2) 24, 429, 434 (1881).

(21) Jacobson, *Cent.* 1898, II 36. (22) Orton, Smith, *J. Chem. Soc.* 87, 395-396 (1905). (23) Réverdin, Crepeux, *Ber.* 36, 3268 (1903). (24) Carstangen, *Ber.* 2, 633 (1869). (25) Woskresenski, *J. prakt. Chem.* (1) 18, 420 (1839). (26) Conant, *J. Am. Chem. Soc.* 49, 293-297 (1927). (27) Kvalnes, *J. Am. Chem. Soc.* 56, 667-670 (1934). (28) Schuloff, *Austrian* 127,813, April 25, 1932, *Cent.* 1932, II 924, *C.A.* 26, 4348 (1932). (29) Levy, Schütz, *Ann.* 210, 154 (1881). (30) Andresen, *J. prakt. Chem.* (2) 28, 422-427 (1883).

(31) Graebe, *Ann.* 146, 55-59 (1868). (32) Jackson, Grundley, *Am. Chem. J.* 17, 653-654 (1895). (33) Lang, Baker, *J. Chem. Soc.* 63, 1322-1323 (1893). (34) Brass, Papp, *Ber.* 53, 458 (1920). (35) Niemeyer, *Ann.* 225, 337-338 (1885). (36) Schönberg, Ismail, *J. Chem. Soc.* 1910, 1374-1378.

3:4675 3-CHLORO-4-HYDROXYBENZOIC ACID



$C_7H_5O_3Cl$

Beil. X - 175  
X<sub>1</sub>—

M.P. 169-176° (1) (2)

169° (3)

165-166° (4)

164-165° (5)

164° (6)

Colorless ndls. from aq.; spar. sol. cold but eas. sol. hot aq.; eas. sol. alc., ether; very eas. sol. acetone; spar. sol.  $C_6H_6$ ,  $CHCl_3$ , lgr. — Sublimes undecomposed. [For study of ioniz. const. at 25° see (9).]

[For prepn. of  $\bar{C}$  from p-hydroxybenzoic acid (1:0846) with aq. HCl + 30%  $H_2O_2$  (60-90% yield (6)) or in  $Na_2CO_3$  soln. with  $Cl_2$  (100% yield  $Na\bar{A}$  (7)), or in AcOH with  $KClO_3$  + HCl (8), or with  $SbCl_5$  on warming (1), see indic. refs.; from 3-amino-4-hydroxybenzoic acid [Beil. XIV-597] via diazotization and use of  $Cu_2Cl_2$  reactn. see (4); from o-chlorophenol (3:5980) in  $CCl_4$  with alc. alk. in s.t. at 125-130° see (5); from methyl 3-chloro-4-hydroxybenzoate (see below) by hydrol. with 40% KOH see (2); from 3-chloro-4-hydroxybenzonitrile (3) via hydrol. with acid see (5).]

$\bar{C}$  in aq. soln. gives with  $FeCl_3$  a brown ppt. (1).

[ $\bar{C}$  with  $PCl_5$  (2 moles) followed by treatment of the intermediate acid chloride with aq. yields (1) 3,4-dichlorobenzoic acid (3:4925);  $\bar{C}$  on warming with  $SbCl_5$  (2 moles) yields (1) 3,5-dichloro-4-hydroxybenzoic acid (3:4950).]

[For studies of bactericidal actn. of  $\bar{C}$  or its derivatives see (10) (11) (12) (13) (14) ]



③ Methyl 3-chloro-4-hydroxybenzoate: ndls. from dil. alc. or lgr., m.p. 107° (2), 106-107° (4). [From  $\bar{C}$  in MeOH with  $H_2SO_4$  (4) or from methyl *p*-hydroxybenzoate (1:1549) with  $SO_2Cl_2$  (2).] [For reactn. of this prod. with acetobromglucose see (10); for studies of bactericidal power see (11).]

— Ethyl 3-chloro-4-hydroxybenzoate: ndls. from dil. alc., m.p. 77-78° (2). [From ethyl *p*-hydroxybenzoate (1:1534) with  $SO_2Cl_2$  (2); for use as disinfectant see (14).]

— 3-Chloro-4-methoxybenzoic acid (3-chloroanisic acid): scales from dil. AcOH, m.p. 214-215° (16), 213° (4) (15), 212-214° (17). [Prepd. indirectly from 3-chloro-4-methoxybenzamide with  $HNO_2$  (15), from 3-chloro-4-methoxytoluene by oxidn. with  $CrO_3/AcOH$  (16) or alk.  $KMnO_4$  (17).]

— 3-Chloro-4-hydroxybenzamide: ndls. from acetone + ether, m.p. 181-182° (3). [Prepd. indirectly from 3-chloro-4-hydroxybenzonitrile with dil.  $H_2SO_4$  at 160° (3).]

3:4675 (1) Lossner, *J. prakt. Chem.* (2) 13, 432-435 (1876). (2) Mazzars, *Gazz. chim. ital.* 29, I 385-387 (1899). (3) Biltz, *Ber.* 37, 4035-4036 (1904). (4) von Auwers, *Ber.* 36, 1473-1474 (1897). (5) Hasse, *Ber.* 10, 2192-2194 (1877). (6) Leulier, Pinet, *Bull. soc. chim.* (4) 41, 1364-1365 (1927). (7) Tishchenko, *J. Russ. Phys.-Chem. Soc.* 60, 153-162 (1928); *Cent.* 1928, II 768; *C.A.* 22, 3397 (1928). (8) Chem. Fabrik von Heyden, *Ger.* 69,115; *Friedländer* 3, 847. (9) Coppadoro, *Gazz. chim. ital.* 32, I 554 (1902). (10) Sabalitschka, *Arch. Pharm.* 267, 675-685 (1929).

(11) Sabalitschka, *Ber.* 56, 3060 (1926).  
I 2670-2671; *C.A.*  
II 271. (14) Sabalitschka, Böhn, *Ger.* 592,826, Sept. 11, 1930; *Cent.* 1934, I 3369. (15) Gattermann, *Ber.* 32, 1118, 1121 (1899). (16) Schall, Dralle, *Ber.* 17, 2529 (1884). (17) Peratoner, Vitale, *Gazz. chim. ital.* 28, I 217 (1898).

3:4680 8-CHLORONAPHTHOIC  
ACID-1



$C_{11}H_7O_2Cl$

Beil. IX - 651  
IX-1-(276)

M.P. 171-171.5° (1)  
170-170.5° (1)  
169-170° (2)  
168-169° (3)  
167-108° (3)  
167° (4) (5)

Cryst. from  $C_6H_6$  (2), scales from alc. (4). — Subl. in ndls. (4).

[For prepn. of  $\bar{C}$  from naphthalic acid (1:0890) via conv. with  $Hg(OAc)_2$  to anhydro-8-hydroxymercuri-1-napbthoic acid and subsequent reactn. with  $Cl_2$  in AcOH see (1) (3) (6) (7) cf. (8); from 8-aminonaphthoic acid-1 [Beil. XIV-534, XIV-1-(623)] via diazotization and reactn. with  $CuCN$  see (4); from  $\alpha$ -naphthoic acid (1:0785) with  $Cl_2$  in AcOH contg.  $I_2$  see (4); from 8-nitronaphthoic acid-1 [Beil. IX-653] (3) with  $SOCl_2$  in  $C_6H_6$  (some dichloronaphthostyryl also being formed) see (3); from 8-chloro-1-naphthonitrile (see below) by hydrolysis see (9); from 8-chloro-1-naphthoamide (see below) by hydrolysis with  $AcOH/H_2SO_4 + NaNO_2$  see (5) (2).]

$\bar{C}$  with  $Cl_2$  in AcOH contg.  $I_2$  yields (4) (1) 5,8-dichloronaphthoic acid-1 [Beil. IX-651], scales from alc., m.p. 186-187° (4) (1).

$\bar{C}$  with  $PCl_5$  yields (5) 8-chloro-1-napbthoyl chloride (props. not reported).

$\bar{C}$  with cold red fuming  $HNO_3$  yields (10) (11) 8-chloro-5-nitronapbthoic acid-1, lfts. or ndls. from alc., m.p. 227° (10), 225-226° (11). [This prod. with Cu bronze in boilg. toluene for 3 hrs. yields (11) 5-nitronapbthoic acid-1 [Beil. IX-652], m.p. 241-242°.

Salts.  $CaA_2 \cdot 2H_2O$ ; ndls. sol. in 42 pts. cold aq. (4).

— Methyl 8-chloro-1-naphthoate: oil, b.p. 188-189° at 16.2 mm. (2). [From  $\bar{C}$  with ethereal diazomethane (2).]

④ Ethyl 8-chloro-1-naphthoate: ndls. from alc., m.p. 50° (4), 49-50° (5). [From dry  $Ag\bar{A}$  with  $EtI$  at 100° (4) or from acid chloride (above) with  $NaOEt$  (5).] [For reactn. of this ester with Cu bronze at 290° yielding diethyl 1,1'-binaphthyl-8,8-dicarboxylate, m.p. 183°, see (5) (9); for reactn. of the ester with 1-bromonaphthalene + Cu bronze at 290° yielding ethyl 1,1'-binaphthyl-8-carboxylate, m.p. 146°, see (9); for reactn. of this ester with 2-bromonaphthalene + Cu at 290° yielding ethyl 1,2'-binaphthyl-8-carboxylate, m.p. 105°, see (9).]

— 8-Chloro-1-naphthonitrile: ndls. from  $MeOH$ , m.p. 150-151° (9), 145-146° (2), b.p. 200° at 18 mm. (9), 242-244° at 15.5 mm. (7) (2). [From 8-chloronaphthylamine-1 [Beil. XII-1256] via diazotization and reactn. with  $CuCN$  (yields: 57% (5), 22% (2)) (9).]

— 8-Chloro-1-naphthoamide: ndls. from alc., m.p. 203.5° (5). [From the nitrile (above) by hydrolysis with  $AcOH/H_2SO_4$  (5).]

3:4680 (1) Whitmore, Fox, *J. Am. Chem. Soc.* 51, 3363-3367 (1929). (2) Bergmann, Hirschberg, *J. Chem. Soc.* 1936, 334. (3) Rule, Barnett, *J. Chem. Soc.* 1932, 175-179. (4) Eckstrand, *J. prakt. Chem.* (2) 38, 150-151 (1888). (5) Kalb, *Ber.* 47, 1726-1728 (1914). (6) Corbellini, Barbari, *Giorn. chim. ind. applicata* 15, 335-337 (1933). *Cent.* 1933, II 2318; *C A* 27, 5737 (1933). (7) Corbellini, *Ital.* 832,963, May 19, 1934, *Cent.* 1937, I 2460. (8) Leuck, Perkins, Whitmore, *J. Am. Chem. Soc.* 51, 1831-1836 (1929). (9) Meisenheimer, Beisswenger, *Ber.* 65, 32-42 (1932). (10) Eckstrand, *J. prakt. Chem.* (2) 38, 253-254 (1888). (11) Rule, Pursell, Brown, *J. Chem. Soc.* 1934, 168-171.

3:4690 2,5-DICHLOROHYDROQUINONE  
(p-Dichlorohydroquinone)



$C_6H_4O_2Cl_2$  Beil. VI - 850  
VI—  
VI<sub>2</sub>-(845)

M.P. 172° (1) (2)  
170° (3)  
166° (4)

[See also 2,5-dichlorobenzoquinone-1,4 (3:4470).]

Colorless ndls. from boilg. aq., tbs. from  $C_6H_6$ , mechmic pr. from acetone; spar. sol. cold aq, sol. boulg. aq, very eas. sol. alc., ether, or warm  $AcOH$ . — Sublimes in ndls.

[For prepn. of  $\bar{C}$  from 2,5-dichlorobenzoquinone-1,4 (3:4470) by reductn. with  $SO_2$  see (5); from chlorobenzoquinone-1,4 (3:1109) with hot conc.  $HCl$  (83% yield (6)) (4) or in  $CHCl_3$  with  $HCl$  gas (4) see indie. refs.; from hydroquinone (1:1590) with  $HCl + KClO_3$  (2) (7), in  $AcOH$  or better  $CHCl_3$  with  $Cl_2$  (poor yield together with 2,3-isomer) (6), or in  $MeOH$  with  $Cl_2$  (8) see indie. refs.; from chlorohydroquinone (3:3130) with  $HCl + KClO_3$  (68% yield) see (9), from 2,5-dichloro-p-aminophenol (10) by diazotization in  $H_2SO_4 + ZnSO_4$  soln. and hydrolysis of the diazonium salt (10).]

[For use of  $\bar{C}$  as an antioxidant and gum inhibitor in cracked gasoline see (11); for use in aq. petroleum emulsion as insecticidal oil spray see (12); for use as vulcanization accelerator see (19).]

$\bar{C}$  on oxdn. with  $K_2Cr_2O_7$  or  $Na_2Cr_2O_7 + dil. H_2SO_4$  (7) (2) (9) (13) (14) or even with conc.  $HNO_3$  at ord. temp. (4) yields 2,5-dichlorobenzoquinone-1,4 (3:4470) q.v. — [For studies of oxdn.-reductn. potential of system  $\bar{C} +$  corresp. quinone see (9) (15) (16).]

- ① 2,5-Dichlorohydroquinone diacetate: colorless ndls. from dil. alc., m.p. 141° (4) (17). [From  $\bar{C}$  with  $Ac_2O$  (4) or from 2,5-dichlorobenzoquinone-1,4 (3:4470) in  $Ac_2O$  +  $AcOH$  with  $Zn$  dust (17).]
- ② 2,5-Dichlorohydroquinone dihenzoate: colorless wooly ndls. from  $CS_2$ , m.p. 185° (4). [From  $\bar{C}$  on refluxing with  $BzCl$  (4).]
- ③ 2,5-Dichlorohydroquinone dimethyl ether: colorless ndls., m.p. 125° u.c. (17), 123-127° (6), h.p. 261-263° u.c. at 744 mm. (16). [From  $\bar{C}$  in dil. aq.  $NaOH$  on shaking with  $Me_2SO_4$  (63% yield (5)), or from hydroquinone dimethyl ether in  $AcOH$  with  $Cl_2$  (17) (18).] [This prod. with fung.  $HNO_3$  in cold does not nitrate but oxidizes to 2,5-dichlorobenzoquinone-1,4 (3:4470) (17).]

3:4690 (1) Krafft, *Ber.* 10, 800 (1877). (2) Ling, *J. Chem. Soc.* 61, 558 (1892). (3) Fels, *Z. Krist.* 37, 481 (1903). (4) Levy, Schultz, *Ann.* 210, 148-150 (1881). (5) Städler, *Ann.* 69, 312-318 (1849). (6) Eckert, Endler, *J. prakt. Chem.* (2) 104, 83-84 (1922). (7) Hammick, Hampson, Jenkins, *J. Chem. Soc.* 1939, 1264. (8) Plazek, *Roczniki Chem.* 10, 761-776 (1930); *Cent.* 1931, I 1428; *C.A.* 25, 1504 (1931). (9) Conant, Fieser, *J. Am. Chem. Soc.* 45, 2205-2206 (1923). (10) Skraup, Steinruck (to Rheinische Kamfer-Fabrik), *Ger.* 431,513, July 10, 1926; *Cent.* 1926, II 1462.

(11) Clarke, Towne (to Texas Co.), U.S. 2,023,871, Dec. 10, 1935; *Cent.* 1936, I 2671; *C.A.* 30, 851 (1936). (12) Yates (to Shell Development Co.), U.S. 1,778,240, Oct. 14, 1930; *Cent.* 1931, I 2799; *C.A.* 24, 5928 (1930). (13) Kehrman, Grah, *Ann.* 303, 12-14 (1898). (14) Hantzsch, Schniter, *Ber.* 20, 2279-2282 (1887). (15) Hunter, Kvalnes, *J. Am. Chem. Soc.* 54, 2874-2875, 2878 (1932). (16) Kvalnes, *J. Am. Chem. Soc.* 56, 667-670 (1934). (17) Kohn, Gurewitsch, *Monatsh.* 50, 135-136 (1930). (18) Habermann, *Ber.* 11, 1034-1035 (1878). (19) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; *Cent.* 1933, II 3134.

3:4700 4-CHLORO-2-METHYLBENZOIC  
ACID



$C_8H_7O_2Cl$

Beil. IX-468  
IX-

M.P. 172°	(1)
171-172°	(10)
171°	(2)
170° u.c.	(3) (8)
169-170°	(4)
169°	(5)
166-168°	(6)
166°	(7)

Colorless ndls. from nq. alc., dil.  $AcOH$  or  $C_6H_6$ ; eas. sol. hot aq.; eas. volatile with steam. [For prepn. of  $\bar{C}$  from 4-chloro-1,2-dimethylbenzene (3:8675) by oxidn. with boilg. dil.  $HNO_3$  ( $D = 1.20$ ) (7) or with 20 pts. dil.  $HNO_3$  ( $D = 1.10$ ) in s.t. at 160° for 5-6 hrs. (8) (by this method  $\bar{C}$  is always accompanied by the isomeric 5-chloro-2-methylbenzoic acid (3:4670) separable by its less sol. calcium salt (1) (8) (7)) see indic. refs.; from 4-chloro-2-methylbenzaldehyde [Beil. VII-296] by air oxidn. see (4); from chloromethyl 4-chloro-2-methylphenyl ketone (4-chloro-2-methylphenacyl chloride) [Beil. VII-306] by oxidn. with  $KMnO_4$  see (2); from  $\beta$ -chloroethyl 4-chloro-2-methylphenyl ketone (5) by oxidn. at 100° with mixt. of equal pts. conc.  $HNO_3$  and aq. see (5); from 4-chloro-2-methylbiphenyl (3) by oxidn. with  $CrO_3/AcOH$  (8% yield) see (3); from 1-methyl-1-(trichloromethyl)cyclohexadiene-2,5-one-4 [Beil. VII-149] by treatment with  $PCl_5$  giving 4-chloro-2-methylbenzotrichloride, followed by alk. hydrolysis of the latter, see (9); from 4-chloro-2-methylbenzonitrile, m.p. 67° (1) (10), by boilg. for 16 hrs. with 8% nq.  $KOH$  see (1) (10).]

$\bar{C}$  on oxidn. with alk.  $\text{KMnO}_4$  (7) or with 10-20 pta. chl.  $\text{HNO}_3$  ( $D = 1.13$ ) in s.t. at 180-200° for 5 hrs. (1) yields 4-chlorophthalic acid (3:4390).

$\bar{C}$  fused with  $\text{KOH}$  yields (7) 4-hydroxy-2-methylbenzoic acid [Beil. X-215], m.p. 172-173° (7).

Salts.  $\text{NH}_4\bar{A}$ , eas. sol. aq.;  $\text{K}\bar{A} \cdot \text{H}_2\text{O}$ , very eas. sol. aq.;  $\text{Ca}\bar{A}_2 \cdot 3\text{H}_2\text{O}$  more sol. in aq. than corresp. salt of 5-chloro-2-methylbenzoic acid (3:4670);  $\text{Ba}\bar{A}_2 \cdot 4\text{H}_2\text{O}$ , more eas. sol. aq. than calcium salt (for details see (1)).

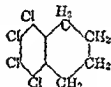
— Methyl 4-chloro-2-methylbenzoate: unrecorded.

— Ethyl 4-chloro-2-methylbenzoate: oil, b.p. 258° (1),  $D_4^{20} = 1.1626$  (10),  $n_D^{20} = 1.52705$  (10) [From  $\bar{C}$  in EtOH with  $\text{HCl}$  gas (1) or from the amide (see below) with ethyl nitrite in s.t. at 140° for 4-5 hrs. (1)]

— 4-Chloro-2-methylbenzamide: colorless ndls. from hot aq., from alc. or ether, m.p. 183° (1). [Obtd. indirectly by partial sapon. of corresp. nitric (above) (1).]

3:4700 (1) Claus, Stapelberg, *Ann.* 274, 287-291 (1893). (2) Kuncell, *Ber.* 41, 2648 (1908). (3) Huntress, Seikel, *J. Am. Chem. Soc.* 61, 820 (1939). (4) von Auwers, Keil, *Ber.* 38, 1896 (1905). (5) Mayer, Müller, *Ber.* 60, 2281 (1927). (6) Mayer, Albert, Schön, *Ber.* 63, 1295-1299 (1933). (7) Krüger, *Ber.* 19, 1757 (1885). (8) Claus, Bayer, *Ann.* 274, 308 (1893). (9) von Auwers, Jülicher, *Ber.* 55, 2167-2168, 2179-2180 (1922). (10) von Auwers, Harres, *Z. physik. Chem.* A-143, 15-16, 18 (1929).

3:4703 6,6,7,8-TETRACHLORO-1,2,3,4-TETRAHYDRONAPHTHALENE  
(5,6,7,8-Tetrachlorotetralin)



$\text{C}_{10}\text{H}_6\text{Cl}_4$  Beil. V —  
V<sub>1</sub> —  
V<sub>2</sub>-(386)

M.P. 172° (1) B.P. 180° at 26 mm. (1)  
174° (2)

[See also naphthalene tetrachloride (3:4750).]

Cryst. from AcOH.

[For prepn. of  $\bar{C}$  from 1,2,3,4-tetrahydronaphthalene (tetralin) (1:7550) with  $\text{Cl}_2$  in pres. of  $\text{I}_2$  (15% yield (2)) at 15° in diffuse daylight see (1) (2); for formn. in small amt. from tetralin during prepn. of 7-chloro-1,2,3,4-tetrahydronaphthalene ( $\beta$ -chlorotetralin) with  $\text{Cl}_2$  in pres. of  $\text{I}_2$  at 10° see (1).]

$\bar{C}$  with  $2\text{Br}_2$  in boulg.  $\text{CS}_2$  yields (1) 1,2-dibromo-5,6,7,8-tetrachloronaphthalene [Beil. V<sub>2</sub>-(388)], m.p. 142° (1), which with alc. (7)  $\text{NaOEt}$  gives (alm. quant. yield (1)) 1,2,3,4-tetrachloronaphthalene [Beil. V<sub>2</sub>-(446)], m.p. 198°

3:4703 (1) von Braun, *Ber.* 56, 2337 (1923). (2) Wynne, *J. Chem. Soc.* 1946, 61.

3:4704 3-CHLORONAPHTHOQUINONE-1,2  
(3-Chloro- $\beta$ -naphthoquinone)



$\text{C}_{10}\text{H}_6\text{O}_2\text{Cl}$  Beil. VII-720  
VII<sub>1</sub> —

M.P. 172° (1) (2) (3)

Red ndls. from  $\text{CHCl}_3$  — Sol. hot alc., AcOH,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ .

[For prepn. of  $\bar{C}$  from  $\beta$ -naphthol (1:1540) by conversion with  $\text{Cl}_2$  in AcOH (2) to 1,1,3,4-tetrachloro-2-keto-1,2,3,4-tetrahydronaphthalene [Beil. VII-371] (lfts. of monohydrate from aq., m.p. 90-91°; anhydrous lfts. or ndls. from hot lgr., m.p. 101-103°)

followed by treatment with aq.  $\text{Na}_2\text{CO}_3$  (2) (3) (overall yield of  $\bar{\text{C}}$  is 56% (4)). — For prepn. of  $\bar{\text{C}}$  from naphthoquinone-1,2 (1:0062) with  $\text{Cl}_2$  in AcOH (1) (5), or from 1,3-dichloronaphthol-2 (3:1900) by oxidn. with conc.  $\text{HNO}_3$  in AcOH (3), see indic. refs.]

$\bar{\text{C}}$  on reduction with  $\text{SO}_2$  in AcOH gives (1) 3-chloro-1,2-dihydroxynaphthaleno [Beil. VI-975], colorless ndls., m.p. 116–117° (1).

$\bar{\text{C}}$  on oxidn. with aq.  $\text{Ca}(\text{OCl})_2$  undergoes rupture of the quinoid ring and a subsequent series of changes (5) resulting in formation of (plithalidyl-3)-dichloroacetic acid [Beil. XVIII-419], tbls. of monohydrate from aq., anhydrous ndls. from  $\text{C}_6\text{H}_6$ , m.p. 157°, accompanied by some 2,2-dichloroindandione-1,3 [Beil. VII-096, VII-1-(375)], m.p. 124–125°.]

$\bar{\text{C}}$  although insol. in aq.  $\text{Na}_2\text{CO}_3$  gradually dissolves in dil. aq. alkali with conversion (1) to 3-chloro-2-hydroxy-naphthoquinone-1,4 (3-chloro-4-hydroxynaphthoquinone-1,2) [Beil. VIII-301], yel. ndls. from alc., m.p. 215°.]

$\bar{\text{C}}$  with alc.  $\text{NH}_3$  on htg. gives (1) 3-chloro-2-hydroxynaphthoquinone-1,4-imine-4 (3-chloro-4-aminonaphthoquinone-1,2) [Beil. VIII-305], m.p. abt. 200°.]

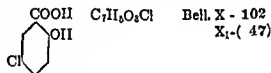
$\bar{\text{C}}$  with alc. aniline on htg. similarly gives (1) 3-chloro-2-hydroxynaphthoquinone-1,4-anil-1 (3-chloro-4-anilino-naphthoquinone-1,2) [Beil. XII-225], yel. ndls. from AcOH, m.p. 253°.]

$\bar{\text{C}}$  with 2,3-dimethylbutadiene-1,3 (1:8050) in spec. purified  $\text{CHCl}_3$  in s.t. at 100° in dark for 1 hr. readily forms (70% yield (4)) a Diels-Alder type adduct  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Cl}$ , lemon-yel. ndls. from ether/pet. ether, m.p. 87–88°; this adduct is unstable even at 10° and in alc. or ether soln. on shaking with air loses  $\text{HCl}$  and is oxidized (by loss of 2 hydrogen atoms) giving (87% yield (4)) 2,3-dimethylphenanthraquinone, m.p. 237–238° u.c., 242–243° cor. (4). — For study of reaction of  $\bar{\text{C}}$  with excess 2,3-dimethylbutadiene-1,3 (1:8050) giving 36% yield of a halogen-free prod. of m.p. 135° see (6).

— 3-Chloronaphthoquinone-1,2-oxime-1 (3-chloro-1-nitrosonaphthol-2) [Beil. VII-721]; yel.-red ndls. from hot alc., m.p. 167–168° dec. (7). [Prepd. indirectly.]

3:4704 (1) Zincke, *Ber.* 19, 2407 (1880). (2) Zincke, *Kegel, Ber.* 21, 3550–3552 (1888). (3) Zincke, *Kegel, Ber.* 21, 3380, 3380 (1888). (4) Fieser, Dunn, *J. Am. Chem. Soc.* 59, 1019–1020 (1937). (5) Zincke, Schmidt, *Ber.* 27, 737–739 (1894). (6) Fieser, Dunn, *J. Am. Chem. Soc.* 59, 1021–1021 (1937). (7) Zincke, Schmunk, *Ann.* 257, 140–145 (1890).

3:4705 5-CHLORO-2-HYDROXYBENZOIC  
ACID  
(5-Chlorosalicylic acid)



M.P. [176°	(1)]	M.P. (contd.) 171–172.5°	(10)
173°	(2)	170–171°	(11)
172.5°	(3)	108°	(12) (13)
172–173°	(4)	107.5°	(14) (15) (16)
172°	(5) (6) (7) (8)	107–108°	(17) (18) (19)
	(9) (22) (27)		

Colorless ndls. from aq. or alc.; sol. in 1100 pts. aq. at 20° and in 80 pts. aq. at 100° (17); cas. sol. alc., ether,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ , AcOH; spar. sol. lgr. — Volatile with steam (12). — Shows sternutatory props.

[For prepn. of  $\bar{\text{C}}$  from *p*-chlorophenol (3:0475) in  $\text{CCl}_4$  with aq.  $\text{NaOH}$  (very small yield (15)) in pres. of  $\text{Cu}$  (19) or in  $\text{CCl}_4$  with alc.  $\text{KOH}$  in s.t. at 140° for 5–6 hrs. (17) see indic. refs.; from dry sodium *p*-chlorophenolate with  $\text{CO}_2$  at 140–150° under press. see (12) (20); from salicylic acid (1:0780) with  $\text{Cl}_2$  in  $\text{CS}_2$  (65% yield (38)) (3), in MeOH (21) or EtOH (22) (much 3,5-dichlorosalicylic acid (3:4935) also being formed), in AcOH (85%

yield (4)) or in nitrobenzene at 50-60° (23), or with  $C_6H_5ICl_2$  in suitable solvents (89% yield (2)), or by hgt. with  $SbCl_5$  (14), or with  $HCl + 30\% H_2O_2$  (56-66% yield (6)), see indic. refs.; from mono K salicylate in aq. with  $Cl_2$  (24) or from di-potassium salicylate with  $KOCl$  (1) (much 3,5-dichlorosalicylic acid (3:4935) being also formed) see indic. refs.]

[For prepn. of  $\bar{C}$  from 5-chloro-2-aminobenzoic acid (5-chloroanthranilic acid) [Beil. XIV-365] with nitrous acid at 50° see (11); from 5-amino-2-hydroxybenzoic acid (5-amino-salicylic acid) [Beil. XIV-579, XIV<sub>1</sub>-(650)] via diazotization and use of  $Cu_2Cl_2$  reactn. (62-71% yield (16)) (25) see indic. refs.; from 5-chloro-2-hydroxybenzonitrile [Beil. X-104] by hydrolysis with  $H_2SO_4$  see (13); from ethyl 5-chloro-2-hydroxybenzoate (see below) by hydrolysis with  $KOH$  see (7) (25), from 5-chloro-2-methoxybenzoic acid (see below) by cleavage with conc.  $HI$  see (10); from chloral-5-chlorosalicylamide (see below) by hydrolysis with 10%  $NaOH$  see (26); from 5-chlorosalicylin by oxidn. with  $K_2Cr_2O_7 + H_2SO_4$  (18) or with  $KMnO_4$  followed by acid hydrolysis (9) see indic. refs.; from 6-chloro-2,3-dimethylchromone (27), 6-chloro-2,3-diphenylchromone (28), or 7-chloro-1,2,3,4-tetrahydroxanthone (5) by alk. hydroly. see indic. refs.]

[For use of various esters of  $\bar{C}$  as mothproofing agents (29), as insecticides (30), or as plasticizers (31) (32) see indic. refs.; for studies of bactericidal power of  $\bar{C}$  see (33) (34); for study of fate of  $\bar{C}$  in animal body see (35)]

[ $\bar{C}$  on electrolytic reduction in aq. alc.  $H_2SO_4$  yields (36) 5-chloro-2-hydroxybenzyl alcohol [Beil. VI-893], m.p. 93° (36);  $\bar{C}$  on reductn. with  $Na/Hg$  as directed (16) yields 5-chloro-2-hydroxybenzaldehyde (3:2800).]

[ $\bar{C}$  with  $PCl_5$  (37) in lgr. (38) yields 4-chloro-2-chloroformylphenylphosphoryl dichloride,  $Cl.CO.C_6H_4Cl.O-P(O)Cl_2$  [Beil. X-103], oil, b.p. 183-184° at 13 mm. (38);  $\bar{C}$  with  $PCl_5$  yields (38) 4-chloro-2-chloroformylphenyl metaphosphite,  $Cl.CO.C_6H_4Cl.O-P:O$  [Beil. X-103], m.p. abt. 55-57°, b.p. 155-156° at 14 mm. (38).]

[ $\bar{C}$  with  $ClSO_3H$  at 50-70° yields (39) 3-chlorosulfonyl-5-chloro-2-hydroxybenzoic acid [Beil. XI<sub>1</sub>-(106)], pr. from  $AcOH$ , m.p. 206-207° (39).]

[ $\bar{C}$  with  $HNO_3 +$  conc.  $H_2SO_4$  at 0° (23), or  $\bar{C}$  on warming with fuming  $HNO_3$  (22), or  $\bar{C}$  in  $AcOH$  treated with 5 pts. fuming  $HNO_3$  in  $AcOH$  (40), yields 5-chloro-3-nitrosalicylic acid [Beil. X-120], pale yel. ndls., m.p. 162-163° (22); note that by loss of  $CO_2$  and further nitration 4-chloro-2,6-dinitrophenol [Beil. VI-260, VI<sub>1</sub>-(128)], yel. ndls. from aq., m.p. 80° (22), is also formed.]

[ $\bar{C}$  in alc. with  $I_2 + HgO$  gives (41) 5-chloro- $\alpha$ -iodo-salicylic acid, colorless ndls. from hot dil. alc., m.p. 224° sl. dec. (41);  $\bar{C}$  in alk. with  $I_2/KI$  yields (25) by loss of  $CO_2$  and further iodination 4-chloro-2,6-diiodophenol [Beil. VI<sub>1</sub>-(112)], yellowish ndls. from alc., m.p. 108° (25) (ethyl ether, m.p. 69°, acetate, m.p. 127.5° (25)).]

$\bar{C}$  in aq. soln. gives with  $FeCl_3$  a violet coloration.

Salts.  $Li\bar{A}$ ,  $2H_2O$  (8);  $Na\bar{A}$  (8) (12),  $K\bar{A}$  (8) all eas. sol. nq;  $Ca\bar{A}_2 \cdot 3H_2O$  (14),  $Ba\bar{A}_2 \cdot 3H_2O$  (11) (12) (14) (17) (18) see indic. refs.;  $Pb\bar{A}_2$  (11),  $Ag\bar{A}$  (12) (18), insol. aq.

Ⓐ Methyl 5-chloro-2-hydroxybenzoate (methyl 5-chlorosalicylate): ndls. from alc., m.p. 50° (1), 48° (7) (12), b.p. 249° sl. dec. (12). [From  $\bar{C}$  in  $MeOH$  with  $HCl$  gas (12), or from  $Ag\bar{A}$  with  $MeI$  (1): also from methyl salicylate (1:1750) by chlorination with methyl *N,N*-dichlorocarbamate in  $AcOH$  (44).]

— Ethyl 5-chloro-2-hydroxybenzoate (ethyl 5-chlorosalicylate): ndls. from alc., m.p. 25° (7). [From ethyl salicylate (1:1755) with  $SO_2Cl_2$  (7).]

Ⓑ 5-Chloro-2-methoxybenzoic acid: ndls. from aq., m.p. 82° (42), 81-82° (10), 80-81° (4). [Obtd. indirectly from 2-methoxybenzoic acid (1:0685) in  $AcOH$  with  $Cl_2$  (4), or from 5-chloro-2-methoxybenzonitrile by alk. hydrolysis (43).]

① 5-Chloro-2-ethoxybenzoic acid: lfts. from dil. alc., m.p. 118° (7).

② 5-Chloro-2-acetoxybenzoic acid: cryst. from  $C_6H_6$ , m.p. 149° (8), 148° (42), 142° (25). [From  $\bar{C}$  with  $AcCl$  (42).]

③ 5-Chloro-2-hydroxybenzamide: lfts. from alc. or  $C_6H_6$ , m.p. 226-227° (26) (13), 223.5-224° (7), 222-223° (8). [From methyl or ethyl 5-chlorosalicylates (above) with alc.  $NH_3$  (7).] [This amide with chloral (3:5210) gives on warming (26) chloral-5-chloro-2-hydroxybenzamide, ndls. from  $C_6H_6$ , m.p. 148-149° dec. (26).]

3:4795 (1) Lassar-Cohn, Schultze, *Ber.* 38, 3800 (1905). (2) Neu, *Ber.* 72, 1511 (1939). (3) Hubner, Brenken, *Ber.* 0, 174 (1873). (4) Hirwe, Rana, Gavankar, *Proc. Indian Acad. Sci. A-8*, 211-212 (1938). (5) Hall, Plant, *J. Chem. Soc.* 1933, 234. (6) Leulier, Pinet, *Bull. soc. chim.* (4) 41, 1363 (1927). (7) Mazzara, *Gazz. chim. ital.* 29, I 340-347 (1899). (8) Smith, *Ber.* 11, 1226-1227 (1878). (9) van Wawern, *Arch. Pharm.* 235, 567-568 (1897). (10) Peratoner, Condorelli, *Gazz. chim. ital.* 28, I 211-212 (1898).

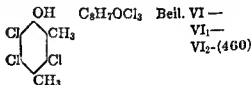
(11) Hubner, Weiss, *Ber.* 6, 175 (1873). (12) Varnholt, *J. prakt. Chem.* (2) 36, 19-22 (1857). (13) Biltz, Steff, *Ber.* 37, 4026-4027 (1904). (14) Beilstein, *Ber.* 8, 810 (1875); *Ann.* 179, 285 Note 2 (1875). (15) Sen, Ray, *J. Indian Chem. Soc.* 9, 176 (1932). (16) Weil, Traun, Marcel, *Ber.* 55, 2664-2665 (1922). (17) Hassé, *Ber.* 10, 2190-2192 (1877). (18) Visser, *Arch. Pharm.* 235, 549-550 (1897). (19) Zeitner, Landau, *Ger.* 258,887, April 17, 1913; *Cent.* 1913, I 1641-1642. (20) Chem. Fabrik von Heyden, *Ger.* 33,635, May 10, 1885, *Friedländer* 1, 234 (1877/87).

(21) Plazek, *Roczniki Chem.* 10, 761-776 (1930); *Cent.* 1931, I 1428; *C.A.* 25, 1504 (1931). (22) Smith, Peirce, *Am. Chem. J.* 1, 176-181 (1879/80); *Ber.* 13, 34-39 (1880). (23) B.A.S.F., *Ger.* 137,118, Nov. 20, 1902, *Cent.* 1902, II 1439-1440. (24) Cahours, *Ann. chim.* (3) 13, 108-111 (1845); *Ann.* 52, 341-342 (1844). (25) Brennans, Girod, *Compt. rend.* 186, 1553-1555 (1928). (26) Hirwe, Rana, *Ber.* 72, 1351-1352 (1939). (27) Simonis, Schuhmann, *Ber.* 50, 1144-1145 (1917). (28) Wittig, *Ann.* 449, 100 (1925). (29) I.G., *Brit.* 274,425, Sept. 7, 1927; *French* 935,973, March 29, 1928; *Cent.* 1929, I 434. (30) I.G., *French* 702,768, April 16, 1931; *Cent.* 1931, II 3530; *Austrian* 125,712, Dec. 10, 1931; *Cent.* 1932, I 2880.

(31) Grether, DuVall (to Dow Chem. Co.), U.S. 2,108,553, April 23, 1940; *C.A.* 34, 5965 (1940). (32) Grether, DuVall (to Dow Chem. Co.), U.S. 2,234,374, March 11, 1941; *C.A.* 35, 8738 (1941). (33) Delauney, *J. pharm. chim.* (8) 25, 254-266, 545-560 (1938, I 2019). (34) Rochaix, Pinet, *Bull. sci. pharmacol.* 34, *C.A.* 22, 443 (1928). (35) Girod, *J. pharm. chim.* (8) 0, *C.A.* 24, 103 (1930). (36) Mottler, *Ber.* 39, 2930 (1900). *Ger.* 89,550; *Friedländer*, 4, 150. (38) Anschütz, Anspach, Bayer and Co., *Ger.* 264,786, Sept. 23, 1913; *Cent.* 1913, II 1350. (40) Ref. 38, pp. 335-339.

(41) Smith, Knerr, *Am. Chem. J.* 8, 05-06 (1886). (42) Anschütz, *Ann.* 367, 263 (1900). (43) Brand, Fabst, *J. prakt. Chem.* (2) 126, 207-208 (1928). (44) Bougault, Chabrier, *Compt. rend.* 213, 400-402 (1941); Chabrier de la Saulniere, *Ann. chim.* (11) 17, 353-370 (1942); *C.A.* 38, 3255 (1944).

3:4707 3,5,6-TRICHLORO-2,4-DIMETHYL-  
PHENOL  
(Trichloro-*m*-4-xenol)



M.P. 174° (1)

Pale yellowish ndls.

[For prepn. of  $\bar{C}$  from 3,5,6-trichloro-2,4-dimethylaniline (1) via diazotization and hydrolysis (yield not stated) see (1).]

[For prepn. of basic Hg and Bi derivs. see (1).]

① 3,5,6-Trichloro-2,4-dimethylphenol methyl ether: m.p. 91.5° (1). [From  $\bar{C}$  with  $Me_2SO_4$  + aq alk. (1).]

② 3,5,6-Trichloro-2,4-dimethylphenol ethyl ether: m.p. 53.5° (1).

③ 3,5,6-Trichloro-2,4-dimethylphenyl acetate: m.p. 86° (1).

— 3,5,6-Trichloro-2,4-dimethylphenyl benzoate: unreported.

3:4707 (1) Bures, Borgmann, *Časopis Českoslov. Lékařnictva*, 7, 270-280 (1927); *Cent.* 1928 I 1171; *C.A.* 22, 4503 (1928).

3:4709 3,4,6-TRICHLORO-2,5-DIMETHYLPHENOL  
(Trichloro-*p*-xylenol)



Beil. VI —

VI<sub>1</sub> —

VI<sub>2</sub>-(467)

M.P. 175° (1)

Pale greenish ndls from alc., AcOH, or pet. eth. or by sublimation — Readily sol. in ether,  $C_6H_6$ , or  $CHCl_3$ , less sol. alc. or other org. solvents; insol. aq. — Volatile with steam.

[For prepn. of  $\bar{C}$  from 3,4,6-trichloro-2,5-dimethylaniline (1), via diazotization and hydrolysis (yield not stated), see (1).]

[For conversion of  $\bar{C}$  to basic Hg or Bi derivs. see (1).]

Ⓐ 3,4,6-Trichloro-2,5-dimethylphenol methyl ether: yellowish ndls from dil. alc. or pet. ether, m.p. 91° (1) [From  $\bar{C}$  with  $Me_2SO_4$  + hot aq. alk. (1).]

Ⓑ 3,4,6-Trichloro-2,5-dimethylphenol ethyl ether: alm. colorless cryst., m.p. 79° (1) [From  $\bar{C}$  with  $Et_2SO_4$  + hot aq. alk. (1).]

Ⓒ 3,4,6-Trichloro-2,5-dimethylphenyl acetate: pr. from alc. + ether, m.p. 103° (1). [From  $\bar{C}$  with  $Ac_2O$  (10 pts.) + trace of  $H_2SO_4$  on hfg. (1).]

Ⓓ 3,4,6-Trichloro-2,5-dimethylphenyl benzoate: hexag. pr. from alc. or pet. ether, m.p. 101° (1) [From  $\bar{C}$  with benzoyl chloride + aq. alk. (1).]

3:4709 (1) Bures, Rubes, *Collection Czechoslov. Chem. Commun.* 3, 648-657 (1929), *C.A.* 24, 1851 (1930) also in *Časopis Českoslov. Lékařnictva*, 8, 225-231, 258-264 (1928); *Cent.* 1929, I 506-507; *C.A.* 23, 3674 (1929).

3:4711 *d,l*- $\alpha,\alpha'$ -DICHLOROSUCCINIC ACID  
(*allo*-Dichlorosuccinic acid;  
isodichlorosuccinic acid)



Beil. II - 619

II<sub>1</sub>-(267)

II<sub>2</sub>-(557)

M.P. 175° u.c. (1) (2) (3) (4) (12)

174-175° dec. (5) (6)

173° (7) (8)

170-172° cor., dec. (9)

170° dec. (10)

[See also *meso*- $\alpha,\alpha'$ -dichlorosuccinic acid (3:4930)]

Cryst. from ether + pet. ether. —  $\bar{C}$  is much more sol. aq. than its *meso* stereoisomer; e.g., 100 cc. satd. aq. soln. of  $\bar{C}$  at 0° conts 54.0 g  $\bar{C}$  (8);  $\bar{C}$  is eas. sol. ether, less so in  $CHCl_3$ .

[For prepn. of  $\bar{C}$  from disodium salt of fumaric acid (1:0895) with  $CCl_4$  in dark or diff. daylight at 5° (yields: 75% (7) 60% (8) 40% (9) 30% (10) (note that as a side reactn. some addn. of chloromaleic acid, and that under some conditions the yield is 10% (9)) from maleic anhydride (1:0625) in  $CCl_4$  by addn. of  $Cl_2$  in sunlight followed by hydrolysis see (12) (9); from *d,l*- $\alpha,\alpha'$ -diaminosuccinic acid [Beil. IV-487, IV<sub>2</sub>-(901)] in aq. HCl soln. with  $NOCl$  see (2); from benzoquinone



dichloride [Beil. VII-573] (13) or toluquinone dichloride [Beil. VII-576] (13) by oxidn. with aq.  $\text{KMnO}_4$  (or  $\text{BaMnO}_4$ ) at  $0^\circ$  see (3); from *d,l*- $\alpha,\alpha'$ -dichlorosuccinyl (di)chloride (3:0395) by aq. hydrolysis see (14)]

$\bar{C}$  behaves as a normal dibasic acid: titration with standard dil. aq. alk. gives Neut. Eq. 93.5. — For study of acid strength ( $K_1 = 372.0 \times 10^{-4}$  at  $16^\circ$ ;  $K_2 = 18.0 \times 10^{-4}$  at  $16.7^\circ$  (8) cf. (15); for study of conductivity see (4).

[Salts (of metals):  $(\text{NH}_4)_2\bar{A} \cdot 2\text{H}_2\text{O}$  (10),  $\text{K}_2\bar{A} \cdot \text{H}_2\text{O}$  (6),  $\text{KH}\bar{A} \cdot 2\text{H}_2\text{O}$  (6),  $\text{CaA} \cdot 2\frac{1}{2}\text{H}_2\text{O}$  (10),  $\text{Ba}\bar{A} \cdot 7\text{H}_2\text{O}$  (10),  $\text{Cu}\bar{A} \cdot 2\frac{1}{2}\text{H}_2\text{O}$  (10), all eas. sol. aq.;  $\text{Sr}\bar{A} \cdot 7\text{H}_2\text{O}$  (10), sol. in 15 pts. aq.;  $\text{Pb}\bar{A} \cdot 3\text{H}_2\text{O}$  (10) spar. sol. aq.]

$\bar{C}$  on boilg. with aq. (12) or with aq.  $\text{KOH}$  (7) (6) or aq. acid (6) loses 1  $\text{HCl}$  yielding chlorofumaric acid (3:4853); for study of rate at  $25^\circ$  see (7) (16).

[ $\text{K}_2\bar{A}$  in aq. soln. maintained at neutrality at  $100^\circ$  yields mainly (6) *d,l*-tartaric acid (1:0550)]

$\bar{C}$  with  $\text{PCl}_5$  (2 moles) gives (100% yield (14)) *d,l*- $\alpha,\alpha'$ -dichlorosuccinyl (di)chloride (3:0395), m.p.  $39^\circ$ .

③ Dimethyl *d,l*- $\alpha,\alpha'$ -dichlorosuccinate: m.p.  $43^\circ$  (see 3:0485).

— Diethyl *d,l*- $\alpha,\alpha'$ -dichlorosuccinate: oil (see 3:9578).

— Acid salt of  $\bar{C}$  with *d,l*- $\alpha$ -phenylethylamine: pr. from aq., m.p.  $149$ – $150^\circ$ , rap. htg. (6); satd. aq. soln. at  $25^\circ$  conts. 18.67 g./liter (6). [For details of resolution of  $\bar{C}$  with opt. act.  $\alpha$ -phenylethylamine see (6) (1); note incidentally that, although m.p. of  $\bar{C}$  is  $175^\circ$ , the m.p. of each of the opt. act. stereoisomeric forms is lower, viz.,  $166$ – $167^\circ$  dec. (6),  $168^\circ$  (1).]

(1892). (14) Lutz, *J. Am. Chem. Soc.* 49, 1110 (1927). (15) Holmberg, *J. prakt. Chem.* (2)

84, 164–165 (1911). (16) Holmberg, *Z. physik. Chem.* 79, 165–167 (1912).

3:4713 2,4,6-TRICHLORO-3,5-DIMETHYLPHENOL  
(Trichloro-*m*-5-xlenol)



$\text{C}_8\text{H}_7\text{OCl}_3$

Beil. S.N. 529

M.P.  $177$ – $178^\circ$  (1)

$175$ – $177^\circ$  (2) (4)

Yellow ndls. from lt. pet.

[For prepn of  $\bar{C}$  from 3,5-dimethylphenol (*m*-5-xlenol) (1:1455) with  $\text{Cl}_2$  in hot  $\text{CCl}_4$  (87% yield (1)) or by action of  $\text{ClSO}_3\text{H}$  + conc.  $\text{HCl}$  +  $\text{H}_2\text{O}_2$  (2) see indic. refs.; for formn. of  $\bar{C}$  from 3,5-dimethylphenol-2,4-bis-(sulfonyl chloride) (2) by preliminary  $\text{KOH}$  hydrolysis followed by action of conc.  $\text{HCl}$  + 30%  $\text{H}_2\text{O}_2$  see (2) cf. (4).]

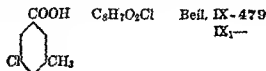
$\bar{C}$  with fuming  $\text{HNO}_3$  is oxidized (64% yield (1)) to 2,6-dichloro-3,5-dimethylbenzoquinone-1,4 (3,5-dichloro-*m*-xyloquinone), yel. lfts, m.p.  $177$ – $178^\circ$  (1),  $178^\circ$  u.c. (3).

[ $\bar{C}$  with  $\text{NaNO}_2$  in  $\text{AcOH}$  at room temp. gives (48% yield (1)) of a mol. cpd. contg. 2 moles  $\bar{C}$  + 1 mole of 2,6-dichloro-3,5-dimethylbenzoquinone-1,4 (above), crimson cubes

from  $\text{CCl}_4$ , becoming yellow at 118–119° without melting, but fusing slowly from 133–164° (1)]

3:4713 (1) Raiford, Kaiser, *J. Org. Chem.* **4**, 565, 567 (1939). (2) Katscher, Lehr, *Monatsh.* **64**, 239–240 (1934). (3) Claus, Runschke, *J. prakt. Chem.* (2) **42**, 124 (1890). (4) Lehr, *Anilin Farben-Ind. (Russ.)* **4**, 77–84 (1934); *Cent.* 1935, I 1365, not in *C.A.*

3:4715 5-CHLORO-3-METHYLBENZOIC  
ACID



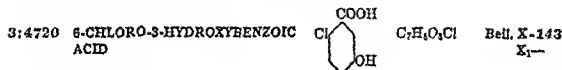
M.P. 178° (1)

Ndls from dil alc.

[For formn. of  $\tilde{\text{C}}$  (in very small yield) from 5-chloro-1,3-dimethylcyclohexadiene-3,5 (5-chloro-1,2-dihydro-*m*-xylene) (Beil. V-119, V<sub>1</sub>-(64)) by oxidn. with boilg. 30%  $\text{HNO}_3$  see (1).]

$\tilde{\text{C}}$  on oxidn. with  $\text{KMnO}_4$  gives (1) 5-chlorobenzenedicarboxylic acid-1,3 (5-chloroisophthalic acid) (3:4960), m.p. 278° (1), together with a little 5-hydroxybenzenedicarboxylic acid-1,3 (5-hydroxyisophthalic acid) [Beil. X-504, X<sub>1</sub>-(257)], m.p. 283°.

3:4715 (1) Klages, Knoevenagel, *Ber.* **23**, 2045–2046 (1895).



M.P. 178–179° (1)

178° (2) (6)

177–178° (3)

176–177° (3)

175° (4)

169–170° (5)

Colorless cryst. from aq. [Ioniz. const. of  $\tilde{\text{C}}$  at 25° =  $1.40 \times 10^{-3}$  (6)].

[For prepn. of  $\tilde{\text{C}}$  from 6-chloro-3-aminobenzoic acid [Beil. XIV-412, XIV<sub>1</sub>-(565)] via diazotization and boilg. with aq. (yield: 60–70% (4) 10% (3)) see indic. refs.; from 6-amino-3-hydroxybenzoic acid [Beil. XIV-591] via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  (?) see (1); from 6-chloro-3-hydroxytoluene (3:1535) via conv. with  $\text{POCl}_3$  to 4-chloro-3-methylphenylphosphoric acid, oxidn. with  $\text{KMnO}_4$  to 4-chloro-3-carboxyphenylphosphoric acid, and finally acid hydrolysis to  $\tilde{\text{C}}$  see (3); for formn. of  $\tilde{\text{C}}$  from methyl ether of  $\tilde{\text{C}}$  (see below) by cleavage with  $\text{HI}$  see (5), from ethyl ester of  $\tilde{\text{C}}$  (see below) by hydrolysis with 35%  $\text{KOH}$  see (2); from *m*-hydroxybenzoic acid (1:0825) with  $\text{Cl}_2$  in  $\text{MeOH}$  (7) or in  $\text{AcOH}$  (1) see indic. refs.]

[ $\tilde{\text{C}}$  on distn. with  $\text{Ba}(\text{OH})_2$  yields (5) *p*-chlorophenol (3:0475).]

[ $\tilde{\text{C}}$  with cinnamic acid (1:0735) in conc.  $\text{H}_2\text{SO}_4$  + a few drops fuming  $\text{H}_2\text{SO}_4$  (18%  $\text{SO}_3$ ) gives (20% yield (3)) anthracoumarin, golden-yel. ndls. from  $\text{AcOH}$  or by sublimation, m.p. 274° (3).]

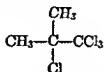
① Methyl 6-chloro-3-hydroxybenzoate: thls. from dil. alc., m.p. 100° (2). [From  $\tilde{\text{C}}$  in  $\text{MeOH}$  with conc.  $\text{H}_2\text{SO}_4$  (2).]

— Ethyl 6-chloro-3-hydroxybenzoate: not specifically characterized. [For formn. (together with the isomeric ethyl 2-chloro-3-hydroxybenzoate) from ethyl *m*-hydroxybenzoate (1:1471) by actn. of  $\text{SO}_2\text{Cl}_2$  see (2).]

— 6-Chloro-3-methoxybenzoic acid: ndls. from AcOH, m.p.  $173.5^\circ$  (9),  $170-171^\circ$  (2) (8). [Prepd indirectly from methyl ester (above) with MeI + MeOH/KOH, followed by hydrolysis with 35% KOH; also from 6-chloro-3-methoxytoluene by oxidn. with  $\text{KMnO}_4$  (5), or from 6-chloro-3-methoxybenzaldehyde by oxidn. with alk.  $\text{KMnO}_4$  (8).]

3:4720 (1) Beyer, *Rec. trav. chim.* **40**, 628 (1921). (2) Mazzara, *Gazz. chim. ital.* **29**, I 376-379 (1899). (3) Minaev, Ripper, *Monatsh* **42**, 76-80 (1921); *J. Russ. Phys.-Chem. Soc.* **54**, 673-679 (1922/23); *Cent.* **1924**, I 905. (4) Minaev, *J. Russ. Phys.-Chem. Soc.* **58**, 113-118 (1926); *Cent.* **1926**, II 2295. (5) Peratoner, Condorelli, *Gazz. chim. ital.* **28**, I 214 (1898). (6) Coppadoro, *Gazz. chim. ital.* **32**, I 547 (1902). (7) Plazek, *Roczniki Chem.* **10**, 761-776 (1930); *Cent.* **1931**, I 1428; *C.A.* **25**, 1504 (1931). (8) Hodgson, Beard, *J. Chem. Soc.* **1926**, 154. (9) Gibson, *J. Chem. Soc.* **1926**, 1428.

3:4725 1,1,1,2-TETRACHLORO-2-METHYLPROPANE



$\text{C}_4\text{H}_5\text{Cl}_4$

Beil. I-126

I<sub>1</sub>—

I<sub>2</sub>—

M.P.  $178.6-179.6^\circ$  (1)

B.P.  $192^\circ$  cor. at 1175 mm. (1)

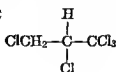
$\bar{\text{C}}$  can be purified by sublimation or by recrystn. from alc.; difficult to separate, however, from 1,2,3-trichloro-2-methylpropane (3:5885), b p  $162-163.1^\circ$  (1). —  $\bar{\text{C}}$  is easily volatile with steam; eas. sol. alc. or ether.

[For formn. of  $\bar{\text{C}}$  (together with other products) from 1,1,2-trichloro-2-methylpropane (3:5710) or from *ter*-butyl chloride (3:7045) with  $\text{Cl}_2$  see (1); for formn. of  $\bar{\text{C}}$  together with other products) from  $\beta,\beta,\beta$ -trichloro-*ter*-butyl alcobol ("Chlorethane") (3:2662) +  $\text{PCl}_5$  see (2).]

$\bar{\text{C}}$  on htg. in s.t. with aq. at  $180^\circ$  yields (3)  $\alpha$ -chloroisobutyric acid (3:0235).

3:4725 (1) Rogers, Nelson, *J. Am. Chem. Soc.* **58**, 1027-1029 (1936). (2) Willgerodt, Dürr, *Ber.* **20**, 539-540 (1887). (3) Willgerodt, Dürr, *J. prakt. Chem.* (2) **39**, 284 (1889).

3:4740 1,1,1,2,3-PENTACHLOROPROPANE  
(unsym.-Pentachloropropane)



$\text{C}_3\text{H}_3\text{Cl}_5$  Beil. I-107

I<sub>1</sub>—

I<sub>2</sub>—

M.P.  $179-180^\circ$  (1)

$178^\circ$  (2)

Colorless ndls. (from hot alc.) with camphoraceous odor. — Sublimes readily. — Insol. aq.; sol. org. solvents. [New comm. prod. (1942) in U.S.A.]

[For prepn. from 1,1,1-trichloropropene-2 (3:5345) by actn. of  $\text{Cl}_2$  in diffuse light see (1).]

[For use as plasticizer with cellulose acetate films see (3).]

3:4740 (1) Victoria, *Rec. trav. chim.* **24**, 282 (1905). (2) Henry, *Rec. trav. chim.* **24**, 342 (1905). (3) Spicers, Ltd., *Hand. Brit.* 279,139, Nov. 17, 1927; *French* 125,165, Aug. 4, 1927; *Cent.* **1928**, I 770.

3:4742 4,5,6-TRICHLORO-2,3-DIMETHYLPHENOL  
(Trichloro-*o*-3-xylene)


 $C_8H_7OCl_3$ 

Boil. VI —  
VI<sub>1</sub> —  
VI<sub>2</sub>-(454)

M.P. 180-181° (1)

Ndls. from dil alc. or lt pet.

[For prepn of  $\bar{C}$  from 5-chloro-2,3-dimethylphenol (5-chloro-*o*-3-xylene) (3:2115) with  $Cl_2$  in lt pet ether see (1).]

— 4,5,6-Trichloro-2,3-dimethylphenyl acetate: unreported.

Ⓒ 4,5,6-Trichloro-2,3-dimethylphenyl benzoate: m.p. 128-129° (1).

3:4742 (1) Hinkel, Collins, Ayling, *J. Chem. Soc.* 123, 2971 (1923).

3:4745 3-CHLORO-2-HYDROXYBENZOIC  
ACID  
(3-Chlorosalicylic acid)


 $C_7H_5O_3Cl$ 

Boil. X - 101  
X<sub>1</sub>-(47)

M.P. 180-182° (1)

180° (2) (6)

178° (3)

170° (4)

Colorless ndls from aq. or dil alc; 100 pts. aq. at 35° dis. 0.8 g.  $\bar{C}$ ; eas. sol. alc., AcOH, or  $CHCl_3$ . — Volatile with steam, sublimes with slight decompn.

[For prepn. of  $\bar{C}$  from *o*-chlorophenol (3:5980) by treatment of dry sodium salt with  $CO_2$  at 140-150° under press. see (3), from 5-sulfo-2-hydroxybenzoic acid (5-sulfosalicylic acid) [Boil. XI-411, XI<sub>1</sub>-(106)] in AcOH with  $Cl_2$  followed by hydrolysis of the resultant 3-chloro-2-hydroxy-5-sulfobenzoic acid with superheated steam (72% yield) see (1); from chloral-3-chlorosalicylamide (see below) by hydrolysis with 10 pts. boilg 10% NaOH for 6 hrs. (86% yield) see (1), for formn. of  $\bar{C}$  from 7-chlorosaccharin (4) by NaOH fusion see (4); for formn. from salicylic acid (1.0780) in  $Na_2CO_3$  soln. with  $Cl_2$  (5-chloro-2-hydroxybenzoic acid (3:4705) is also formed) see (13) ]

[For reactn. of  $\bar{C}$  with methylenedisalicylamide in prepn. of dye intermediates by oxidn. with  $NaNO_2$  see (5) ]

[ $\bar{C}$  on reductn. with Na/Hg in pres. of  $H_3BO_3$  yields (6) cf (7) 3-chloro-2-hydroxybenzaldehyde (3:1010);  $\bar{C}$  with  $ClSO_3H$  at 50-70° yields (8) 5-chlorosulfonyl-3-chloro-2-hydroxybenzoic acid, cryst. from  $CHCl_3$ , m.p. 163-164° (8), which with Zn dust in alc. yields (9) 3,3'-dichloro-4,4'-dihydroxy-5,5'-dicarboxyphenyl disulfide, m.p. 258-259° (9), which in turn with alk.  $Na_2S_2O_4$  undergoes reductive cleavage to 3-chloro-2-hydroxy-5-thiolbenzoic acid (3-chloro-5-thiosalicylic acid), m.p. 210° (9) ]

[ $\bar{C}$  with  $PCl_5$  in low-boilg. pet ether yields (2) 3-chlorosalicyloyl chloride, ndls. from pet ether, m.p. 62-63° (2); this prod. on litg. yields (2) a mixt. of 3-chlorosalicylids:  $\bar{C}$  with  $PCl_5$  yields (2) 6-chloro-2-chloroformylphenyl metaphosphite  $Cl.CO.C_6H_3Cl.O.PO$ , m.p. abt. 65° (2) ]

$\bar{C}$  in aq. soln. gives with  $FeCl_3$  an intense violet color.

Salts.  $Na\bar{A}$  (3),  $K\bar{A}$  (1),  $Ca\bar{A}_2 \cdot 3H_2O$  (1);  $Ba\bar{A}_2 \cdot 3H_2O$  (3),  $Ag\bar{A}$  (1); for details see indic refs.

- Methyl 3-chloro-2-hydroxybenzoate (methyl 3-chlorosalicylate): ndls. from MeOH, m.p. 38° (2), b.p. 259–260° sl. dec. (3). [From  $\bar{C}$  in MeOH with HCl gas (3), or from 3-chlorosalicyloyl chloride (above) in MeOH (2).] [For formn. from methyl salicylate (1:1750) with chloropierin under influence of light see (10) (11).]
- Ethyl 3-chloro-2-hydroxybenzoate (ethyl 3-chlorosalicylate): ndls. from cold alc., m.p. 21° (2), b.p. 269–270° (2), 147° at 12 mm. (2). [From 3-chlorosalicyloyl chloride (above) with EtOH (2).]
- ⑦ 3-Chloro-2-methoxybenzoic acid: white ndls. from alc., m.p. 120–121° (1). [From  $\bar{C}$  in dil. aq. KOH by shaking with  $Me_2SO_4$  in cold, followed by hydrol. of the intermed. ether-ester with bot aq. KOH and subsequent acidif. (1).] — [For nitration with mixt. of  $HNO_3$  ( $D = 1.5$ ) + conc.  $H_2SO_4$  at 20–30° giving (100% yield) 3-chloro-2-methoxy-5-nitrobenzoic acid, m.p. 155.5°, see (14).]
- ⑧ 3-Chloro-2-hydroxybenzamide (3-chlorosalicylamide): white ndls. from dil. alc., m.p. 174–175° (1). [From methyl 3-chlorosalicylate (above) or from 3-chlorosalicyloyl chloride (above) with conc. aq.  $NH_4OH$  in cold (1).] — [This prod. with chloral (3:5210) gives on warming (12) chloral-3-chlorosalicylamide, colorless ndls. from alc., m.p. 159–160° (12) (1), also obt'd. from chloral-salicylamide in AcOH with  $Cl_2$  (1).]
- ⑨ 3-Chloro-2-hydroxybenzanilide (3-chlorosalicylanilide): colorless ndls. from alc., m.p. 158.5–159° (2). [From 3-chlorosalicyloyl chloride (above) with 2 moles aniline in ether soln. (2).]

3:4745 (1) Hirwe, Rana, Gavankar, *Proc. Indian Acad. Sci. A-8*, 208–213 (1935). (2) Anschütz, Anspach, *Ann.* 346, 312–317 (1906). (3) Varnholt, *J. prakt. Chem.* (2) 36, 22–24 (1887). (4) Reissert, Cramer, *Ber.* 61, 2565 (1928). (5) Durand, Huguenin, *Brit.* 183,123, Sept. 6, 1922; *Cent.* 1922, IV 1171. (6) Farbenfabriken vorm. F. Bayer & Co., *Ger.* 228,833, Nov. 22, 1910; *Cent.* 1911, I 51. (7) Farbenfabriken vorm. F. Bayer & Co., *Ger.* 216,305, Nov. 9, 1909; *Cent.* 1909, II 2107. (8) Farbenfabriken vorm. F. Bayer & Co., *Ger.* 264,786, Sept. 23, 1913; *Cent.* 1913, II 1350. (9) British Dyestuffs, Ltd., Saunders, Mendoza, *Brit.* 260,058, Nov. 18, 1926; *Cent.* 1927, I 142. (10) Pinti, *Atti Congr. naz. chim. pura applicata* 1923, 398, 437–438; *Cent.* 1924, I 2514.

(11) Pinti, Badolato, *Atti accad. Lincei* (5) 33, I 475–479; *Cent.* 1924, II 1693. (12) Hirwe, Rana, *Ber.* 72, 1351 (1939). (13) Tischenko, *J. Russ. Phys.-Chem. Soc.* 60, 153–162 (1928); *Cent.* 1928, II 768; *C.A.* 22, 3397 (1928). (14) Davies, Rubenstein, *J. Chem. Soc.* 123, 2851–2852 (1923).

3:4747 2,5,6-TRICHLORO-3,4-DIMETHYLPHENOL  
(Trichloro-o-4-xyleneol)



$C_6H_3OCl_3$

Beil VI —

VI<sub>1</sub>—

VI<sub>2</sub>—(456)

M.P. 182.5° (1)

Ndls. from pet. ether.

[For prepn. of  $\bar{C}$  from 5-chloro-3,4-dimethylphenol (6-chloro-o-4-xyleneol) (3:2705) with  $Cl_2$  in  $CHCl_3$  see (1).]

— 2,5,6-Trichloro-3,4-dimethylphenyl acetate: unreported.

⑦ 2,5,6-Trichloro-3,4-dimethylphenyl benzoate: m.p. 120° (1)

3:4747 (1) Hinkel, *J. Chem. Soc.* 125, 1853 (1924).

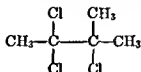


Groth, *Chem. Kristalog.* 5, 368 (1919). (6) Robertson, *Proc. Roy. Soc. (London)* 118-A, 709-727 (1928). (7) Bragg, *Z. Krist.* 66, 27-32 (1927). (8) Kanonnikoff, *J. prakt. Chem.* (2) 31, 342-343 (1885). (9) Leeds, Everhart, *J. Am. Chem. Soc.* 2, 207-209, 210-213 (1880). (10) Laurent, *Ann. chim.* (2) 52, 275-281 (1833); 59, 201-204 (1835).

(11) Paul, Depouilly, *Bull. soc. chim.* (2) 4, 10-12 (1865). (12) Schwarzer, *Ber.* 10, 379 (1877). (13) Fischer, *Ber.* 11, 735-741, 1411-1412 (1878). (14) Krafft, Becker, *Ber.* 9, 1088-1090 (1876). (15) Grimaux, *Bull. soc. chim.* (2) 18, 205-212 (1872); *Compt. rend.* 75, 352-355 (1872). (16) Widman, *Ber.* 15, 2161-2162 (1882). (17) Cleve, *Ber.* 23, 954 (1890). (18) Armstrong, Wynne, *Chem. News* 58, 264-265 (1888). (19) Armstrong, Wynne, *Chem. News* 61, 273, 284 (1890); *Proc. Chem. Soc. (London)* 4, 106 (1888). (20) Helbig, *Ber.* 28, 505-507 (1895).

(21) Laurent, *Ann. chim.* (2) 74, 26-27 (1840); *Ann.* 35, 292-293 (1840). (22) Matter, *Ger.* 317,755, Dec. 29, 1919; *Cent.* 1920, II 601. (23) Matter, *Ger.* 348,069, Jan. 28, 1922; *Cent.* 1922, IV 45. (24) A.G.F.A., *Ger.* 332,391, Feb. 2, 1921; *Cent.* 1921, II 652; *Ger.* 334,710, March 17, 1921; *Cent.* 1921, II 964. (25) Schering-Kahlbaum, Freund, Jordan, *Ger.* 461,358, June 20, 1928; *Cent.* 1929, I 1052, *Brit.* 202,997, Oct. 24, 1924, *Cent.* 1925, I 1456.

### 3:4755 2,3,3-TRICHLORO-2-METHYLBUTANE

C<sub>5</sub>H<sub>9</sub>Cl<sub>3</sub>

Beil. I-135

I<sub>1</sub>—  
I<sub>2</sub>—

M.P. 182-183° (1)

abt. 170° (2)

[For prepn. of  $\bar{C}$  from 2-chloro-2-methylbutane (3:7220) or from 2,3-dichloro-2-methylbutane (3:7975) with Cl<sub>2</sub> see (2); for formn. from 3-chloro-2-methylbutene-2 (3:7335) + Cl<sub>2</sub> (10% yield together with other prods.) see (1) (an earlier product (3) obtd by this latter method and to which this structure was assigned was reported as a liquid, b.p. 176°,  $D_4^{25} = 1.215$ ,  $n_D^{25} = 1.472$ ).]

$\bar{C}$  is not (2) saponified by 20% aq. K<sub>2</sub>CO<sub>3</sub>.

$\bar{C}$  on htg. with 2 moles quinoline at 195-225° gives (60% yield (2))  $\beta$ -chloroisoprene (3:7290).

3:4755 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, II 4223, C.A. 33, 4190 (1939). (2) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 6, 1116-1132 (1936); *Cent.* 1937, I 573; C.A. 31, 1003 (1937). (3) Brochet, *Ann. chim.* (7) 10, 385 (1897).

### 3:4775 3,4-DICHLORONAPHTHO-QUINONE-1,2

C<sub>10</sub>H<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub>Beil. VII-721  
VII<sub>1</sub>—

M.P. 184-185° (1)

184° (1) (2) (3)

183° (6)

Red tbls. or ndls from AcOH, C<sub>6</sub>H<sub>6</sub> or CHCl<sub>3</sub>. — Spar. sol. alc., fairly eas. sol. CHCl<sub>3</sub>. — Sublimes undecomposed.

[For prepn. of  $\bar{C}$  from 1-aminonaphthol-2 hydrochloride [Beil. XIII-676, XIII<sub>1</sub>-(274)], in AcOH with Cl<sub>2</sub> (68.5% yield (3)) (2) (4), or from naphthoquinone-1,2 (1:9062) in AcOH with Cl<sub>2</sub> (2), see indic. refs; for formn. of  $\bar{C}$  from 3,4-dichloro-naphthoquinone-1,2-oxime-1 (3,4-dichloro-1-nitroso-naphthol-2) [Beil. VII-721] on oxidn. with conc. HNO<sub>3</sub> in AcOH soln. see (5); from 3,4-dichloro-3-nitro-1,2-dioxonaphthalene tetrahydride-1,2,3,4 [Beil. VII-701] with AcCl in s.t. at 100° see (6)]

$\bar{C}$  dis. in cold dil. aq. alk. yielding colorless soln. which upon acidification gives (90% yield (4))  $\bar{C}$  acid-3 [Beil. X-325], ndls with 1 H<sub>2</sub>O (from dil.  $\bar{C}$  in oxidn. in dil. aq. or AcOH soln. with CrO<sub>3</sub> gives ndene-1-one-3 ("dichloroindone") [Beil. VII-384], gold-yel. ndls from alc. or AcOH, m.p. 89-90°. [For behavior of  $\bar{C}$  with Ca(OCl<sub>2</sub>) soln see (7).]

$\bar{C}$  with alc. NaOEt yields (8) 3-chloro-4-ethoxynaphthoquinone-1,2, [Beil. VIII-299], or.-red ndls. from alc., m.p. 149° (8)

$\bar{C}$  in hot alc soln. on treatment with alc. NH<sub>3</sub> yields (2) 3-chloro-2-hydroxynaphthoquinone-1,4-imide-4 (4-amino-3-chloronaphthoquinone-1,2) [Beil. VIII-305], m.p. abt. 260° (2)

$\bar{C}$  in dil AcOH with excess SO<sub>2</sub> (2) reduces to 3,4-dichloro-1,2-dihydroxynaphthalene [Beil. VI-975], m.p. 125° (2)

[For cpd. formn. of  $\bar{C}$  with SnCl<sub>4</sub> see (9); for reactn. of  $\bar{C}$  with 2,3-dimethylbutadiene-1,3 in CHCl<sub>3</sub> see (10)]

3:4775 (1) Zincke, *Ann.* 257, 146-147 (1890). (2) Zincke, *Ber.* 19, 2499-2500 (1886). (3) Brass, Mosl, *Ber.* 59, 1271 (1926). (4) Zincke, Engelhardt, *Ann.* 283, 347-349 (1894). (5) Zincke, Schmunk, *Ann.* 257, 146-147 (1890). (6) Zincke, Scharfenberg, *Ann.* 268, 303-304 (1892). (7) Zincke, Schmidt, *Ber.* 27, 744 (1894). (8) Hirsch, *Ber.* 33, 2114 (1900). (9) Brass, Fengler, *Ber.* 64, 1663-1664 (1931). (10) Fieser, Dunn, *J. Am. Chem. Soc.* 59, 1020 (1937).

3:4783 4,5,6-TRICHLOROPYROGALLOL



C<sub>6</sub>H<sub>3</sub>O<sub>3</sub>Cl<sub>3</sub> Beil. VI-1084  
VI<sub>1</sub>-  
VI<sub>2</sub>-

M.P. about 185° dec. (1)  
177° u.c. dec. (2)  
175° (3)

Ndls. with 3 H<sub>2</sub>O, m.p. 75° (1) from alc. or C<sub>6</sub>H<sub>6</sub> (2); this trihydrate in vac. over H<sub>2</sub>SO<sub>4</sub> loses 2 H<sub>2</sub>O, the final H<sub>2</sub>O at 110° (2). —  $\bar{C}$  is spar sol in cold aq., C<sub>6</sub>H<sub>6</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub>, or CS<sub>2</sub>; eas. sol. alc., ether, or hot aq.

[For prepn. of  $\bar{C}$  from pyrogallol (1,2,3-trihydroxybenzene) (1:1555) in 60% AcOH with Cl<sub>2</sub> (2), or with SO<sub>2</sub>Cl<sub>2</sub> in dry ether (3), see indic. refs.]

[For prepn. of  $\bar{C}$  from "leucogallol" [Beil. VI-1078] or "mairogallol" [Beil. VI-1078] by reduction with Zn dust + dil. H<sub>2</sub>SO<sub>4</sub> see (1); from gallic acid (1:0875) in CHCl<sub>3</sub> with Cl<sub>2</sub> see (4)]

[ $\bar{C}$  in CCl<sub>4</sub> or CHCl<sub>3</sub> prev. satd. with Cl<sub>2</sub> gives (2) "leucogallol."]

$\bar{C}$  in ether soln. with aq. Ba(OH)<sub>2</sub> gives deep blue coloration; with aq. Na<sub>2</sub>SO<sub>3</sub> a fugitive red coloration (2).

$\bar{C}$  with aq. FeCl<sub>3</sub> gives (4) a blue coloration.

$\bar{C}$  with conc. HNO<sub>3</sub> is oxidized and decomposed (2);  $\bar{C}$  dis. in cold conc. H<sub>2</sub>SO<sub>4</sub> without evoln. of gas but on warming decomposes (2).

$\bar{C}$  reduces NH<sub>4</sub>OH/AgNO<sub>3</sub> (1)

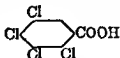
— 4,5,6-Trichloropyrogallol trimethyl ether: cryst. from alc., m.p. 54° (5). [Prepd. indirectly (5)]

125° (4), 122° (1).



3:4782 (1) Hantzsch, Schniter, *Ber.* 20, 2034-2037 (1887). (2) Webster, *J. Chem. Soc.* 45, 205-208 (1884). (3) Peratoner, Condorelli, *Gazz. chim. ital.* 28, I 225-226 (1898). (4) Bietrix, *Bull. soc. chim.* (3) 15, 904-906 (1896). (5) Bartolotti, *Gazz. chim. ital.* 27, I 290-291 (1897).

3:4790 2,3,4,5-TETRACHLORO-  
BENZOIC ACID


 $C_7H_3O_2Cl_4$ 

Bell. IX-346  
IX<sub>1</sub>—

M.P. 186° (1)

Ndls. from alc. — Eas. sol. alc., ether; spar. sol. aq.

[For prepn. of  $\bar{C}$  from tetrachlorophthalic acid (3:4946) by htg. with 2-3 pts. AcOH in s.t. at 300° for 3-4 hrs. see (1); by htg. with steam +  $H_2$  at 200-400° over decarboxylating cat. see (2).]

$\bar{C}$  on  $\frac{1}{2}$  hr. boilg. with mixt. of 2 pts.  $HNO_3$  ( $D = 1.48$ ) + 1 pt. conc.  $H_2SO_4$  gives (100% yield (1)) 2,3,4,5-tetrachloro-2-nitrobenzoic acid [Beil. IX-405], lfts. from aq., but no m.p. has been reported.

Neither the action (if any) of  $PCl_5$  or  $SOCl_2$  on  $\bar{C}$  nor the expected 2,3,4,5-tetrachlorobenzoyl chloride has been recorded.

— Methyl 2,3,4,5-tetrachlorobenzoate: unrecorded.

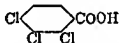
— Ethyl 2,3,4,5-tetrachlorobenzoate: from  $\bar{C}$  + EtOH + HCl gas; ndls. alc., m.p. 31.5° (1).

— 2,3,4,5-Tetrachlorobenzamide: unrecorded.

— 2,3,4,5-Tetrachlorobenzanilide: unrecorded.

3:4796 (1) Tust, *Ber.* 20, 2439-2431 (1887). (2) Jaeger (to Selden Co.), U.S. 1,953,232, April 3, 1934; *Cent.* 1934, II 669; *C.A.* 28, 3743 (1934).

3:4810 2,3,4-TRICHLOROBENZOIC  
ACID


 $C_7H_3O_2Cl_3$ 

Bell. IX-345  
IX<sub>1</sub>—

M.P. 186-187° (1)

Ndls. from hot aq. (1). —  $\bar{C}$  does not melt under boiling water (1).

[For prepn. from 2,3,4-trichlorotoluene (3:0425) by oxidn. with  $HNO_3$  in s.t. at 150° see (1); from 2,3,4-trichlorobenzaldehyde (3:2445) by oxidn. with  $KMnO_4$  see (2).] [The latter product was probably impure (1).]

No further data on  $\bar{C}$  are recorded.

3:4810 (1) Cohen, Dakin, *J. Chem. Soc.* 81, 1328 (1902). (2) Seellg, *Ann.* 237, 150 (1887).

3:4820 3-CHLOROPHTHALIC ACID


 $C_8H_5O_4Cl$ 

Bell. IX - 816  
IX<sub>1</sub>-(360)

M.P. 186-187° (1)

185-187° (2)

186° (3)

184° (4) (5)

[See also 3-chlorophthalic anhydride (3:3900).]

Ndls. from aq.; eas. sol. alc.; eas. sol. ether (use in sepn. from phthalic acid (1:0820) (6). — 100 pts. aq. at 14° dis. 2.16 pts.  $\bar{C}$  (5). — [For sepn. of  $\bar{C}$  from *o*-chlorobenzoic acid (3:4150) by use of  $\text{CHCl}_3$  see (7).]

[For prepn. of  $\bar{C}$  from 3-chlorophthalic anhydride (3:3900) by hydrolysis with boilg. dil.  $\text{HCl}$  see (3) (6); from 1,5-dichloronaphthalene (3:3200) by oxidn. with  $\text{CrO}_3/\text{AcOH}$  see (5); from 5-chloro-1,2,3,4-tetrahydronaphthalene [Beil. V<sub>1</sub>-(237)] (1) by oxidn. with  $\text{KMnO}_4$  see (1); from 3-chloro-2-methylbenzoic acid (3:4435) by oxidn. with  $\text{KMnO}_4$  see (8).]

$\bar{C}$  on htg above its m p yields (5) (8) 3-chlorophthalic anhydride (3:3900).

[ $\bar{C}$  on  $\text{KOH}$  fusion yields (8) (note rearrangement) 4-hydroxyphthalic acid [Beil. X-499, XI<sub>1</sub>-(255)], m p. 204–205°, with conv. to corresp. anhydride, m p. 171°.]

[ $\bar{C}$  with steam passed over cat. at 350° loses  $\text{CO}_2$  presumably yielding (9) *o*-chlorobenzoic acid (3:4150) and/or *m*-chlorobenzoic acid (3:4392).]

[ $\bar{C}$  htd. with  $\text{Hg}(\text{OAc})_2$  in  $\text{AcOH}$  as directed (2) gives *anhydro*-2-hydroxymercuri-3-chlorobenzoic acid which on htg with aq  $\text{HCl}$  yields *m*-chlorobenzoic acid (3:4392).]

Salts.  $\text{Ag}_2\bar{A}$ , ndls. from hot aq. (5);  $\text{Ba}\bar{A}$ , eas. sol. cold aq., but spar. sol. hot aq., on protracted boilg. with aq gives monohydrate which is insol. cold aq. (8).

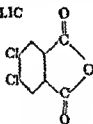
Esters. The neutral dimethyl and diethyl esters of  $\bar{C}$  are unreported; of the various possible acid esters only ethyl hydrogen 3-chlorophthalate, m p. 118–119° (1), has been reported.

3:4830 (1) von Braun, Larbig, Kredel, *Ber.* 56, 2337–2338 (1923). (2) Whitmore, Culhane, *J. Am. Chem. Soc.* 51, 602–605 (1929). (3) Bogert, Boroschek, *J. Am. Chem. Soc.* 23, 751 (1901). (4) Egerer, Meyer, *Monatsh.* 34, 81 (1913). (5) Guareschi, *Gazz. chim. ital.* 17, 120–122 (1887). (6) Smith, *J. Chem. Soc.* 1933, 1643–1644. (7) Jaeger (to Selden Co.), U.S. 1,685,634, Sept. 25, 1928; *Cent.* 1929, 1 807. (8) Krüger, *Ber.* 18, 1759 (1885). (9) Jaeger (to Selden Co.), U.S. 1,953,231, April 3, 1934, *Cent.* 1934, II 1688.

### 3:4830 4,5-DICHLOROPHTHALIC ANHYDRIDE

 $\text{C}_8\text{H}_2\text{O}_3\text{Cl}_2$ 

Beil. XVIII - 483  
XVII<sub>1</sub>-(254)



M.P. 187.5–188° cor. (1) B.P. 313° (4)

187° (2) (3)

185–187° (4)

185° (6)

[See also 4,5-dichlorophthalic acid (3:4890).]

Tbls. or pr. from hot toluene or from  $\text{CCl}_4$ ; spar. sol. cold but eas. sol. hot  $\text{C}_6\text{H}_6$  or toluene; very little sol. in  $\text{CCl}_4$ .

[For prepn. of  $\bar{C}$  from 4,5-dichlorophthalic acid (3:4890) by htg. at 200° (4) or by htg. with  $\text{AcCl}$  (2) see indic. refs.; for formn. of  $\bar{C}$  (together with other isomers) from phthalic anhydride (1:0725) with  $\text{Cl}_2$  in pres. of Fe or Fe salts at 160–200° (5), or from phthalic anhydride (1:0725) or 3-chlorophthalic anhydride (3:3900) with  $\text{Cl}_2$  in fumg.  $\text{H}_2\text{SO}_4$  in pres. of  $\text{I}_2$  (4) (1), see indic. refs.; for formn. of  $\bar{C}$  from aq. solns. of alk. salts of phthalic acid (1:0820) with  $\text{Cl}_2$  see (2) (6) (7).]

[For sepn. of  $\bar{C}$  from isomeric dichlorophthalic anhydrides by means of salts of corresp.

acids, etc., see (4) (8) (1); by means of differential hydrolysis with  $\text{H}_2\text{SO}_4$  (prods. with no  $\alpha$  chlorine such as  $\bar{\text{C}}$  require  $\text{H}_2\text{SO}_4$  of 98–100% concn., those with 1  $\alpha$  chlorine such as 3,4-dichlorophthalic anhydride hydrolyze with 56–95%  $\text{H}_2\text{SO}_4$ , those with 2  $\alpha$  chlorine atoms such as 3,6-dichloro- or 3,4,5,6-tetrachlorophthalic anhydrides hydrolyze at  $\text{H}_2\text{SO}_4$  concns. of less than 50%) see (9).]

$\bar{\text{C}}$  dislvd. in nbs. alc. yields (4) ethyl hydrogen 4,5-dichlorophthalate, ndls. from  $\text{CHCl}_3$ , m.p. 133–134° (4).

[ $\bar{\text{C}}$  with 1 mole  $\text{NH}_2\text{OH} \cdot \text{HCl} + \text{Na}_2\text{CO}_3$  in aq. soln. as directed (4) yields 4,5-dichlorophthaloylhydroxylamine (*N*-hydroxy-4,5-dichlorophthalimide) [Beil. XXI-504], pr. from  $\text{MeOH}$ , m.p. 195–197° dec. (4); this prod. on warming with aq.  $\text{Na}_2\text{CO}_3$  gives 100% yield 4,5-dichloro-2-aminobenzoic acid (4,5-dichloroanthranilic acid) [Beil. XIV-368, XIV-1-(549)], m.p. 213–214° (4).]

[ $\bar{\text{C}}$  with steam passed over cat. nt 380–420° loses  $\text{CO}_2$  presumably yielding (10) 3,4-dichlorobenzoic acid (3:4925).]

$\bar{\text{C}}$  with benzene +  $\text{AlCl}_3$  (12) or in acetylene tetrachloride (11) gives (98% yield (12)) 4,5-dichloro-2-( $\alpha$ -benzoyl)benzoic acid [Beil. XI-(357)], cryst. from  $\text{C}_6\text{H}_6$  (12) or toluene (11), m.p. 209° (12), 208° (11), which on htg with 20 pts. conc.  $\text{H}_2\text{SO}_4$  at 160° for 1 hr. gives (92% yield (12)) (11) 2,3-dichloroanthraquinone [Beil. VII-788, VII-1-(413)], yellowish ndls. from  $\text{AcOH}$ , m.p. 267° cor. (12), 265° (11). — [ $\bar{\text{C}}$  with  $\alpha$ -xylene +  $\text{AlCl}_3$  in acetylene tetrachloride gives (80% yield (11)) 4,5-dichloro-2-(3',4'-dimethylbenzoyl)benzoic acid, cryst. from cyclohexane, m.p. 184° (11), which with 10 pts. conc.  $\text{H}_2\text{SO}_4$  at 100° gives (45% yield (11)) 6,7-dichloro-2,3-dimethylanthraquinone, cryst. from xylene, m.p. 305° (11). —  $\bar{\text{C}}$  with *o*-dichlorobenzene (3:6055) +  $\text{AlCl}_3$  4 hrs. at 100° gives (80% yield (11)) 3,4-dichloro-2-(3',4'-dichlorobenzoyl)benzoic acid, cryst. from  $\text{C}_6\text{H}_6$ , m.p. 183°, which with 12 pts. conc.  $\text{H}_2\text{SO}_4$  6 hrs. at 100° gives mainly 2,3,6,7-tetrachloroanthraquinone, cryst. from *o*-dichlorobenzene, m.p. 348° (11). — For analogous reactns. of  $\bar{\text{C}}$  with naphthalene (13), pyrene (14), or *o*-chlorotoluene (15) see indic. refs.]

[ $\bar{\text{C}}$  with hydroquinone (1:1590) +  $\text{H}_3\text{BO}_3$  htd. nt 190° and afterward treated with hot conc.  $\text{H}_2\text{SO}_4$  at 150–165° (16), or  $\bar{\text{C}}$  with  $\text{AlCl}_3$  +  $\text{NaCl}$  htd. at 200–220° (17), or  $\bar{\text{C}}$  with *p*-chlorophenol (3:0475) htd. with fuming  $\text{H}_2\text{SO}_4$  +  $\text{H}_3\text{BO}_3$  (18) gives (yield: 80% (17), 15% (16)) 6,7-dichloro-1,4-dihydroxyanthraquinone (6,7-dichloroquinizarin) [Beil. VII-452, VIII-1-(716)], red-br. cryst. from xylene, m.p. 295.5° (17), 288° (16), (diacetate, m.p. 125° (16), dimethyl ether, m.p. 168.5° (17)).]

[For use of  $\bar{\text{C}}$  in prepn. of pigments of the copper phthalocyanine type see (19).]

$\bar{\text{C}}$  with  $(\text{NH}_4)_2\text{CO}_3$  htd. at 250° for  $\frac{1}{2}$  hr. (20) yields 4,5-dichlorophthalimide, pl. from alc., m.p. 221° (20) (note that behavior of  $\bar{\text{C}}$  with conc. aq.  $\text{NH}_4\text{OH}$  is different yielding (4) 4,5-dichlorophthalamic acid (not specifically characterized) which with alk.  $\text{NaOCl}$  gives 4,5-dichloro-2-aminobenzoic acid (above)). — [For behavior of  $\bar{\text{C}}$  with hydrazine hydrate in  $\text{AcOH}$  yielding corresp. cyclohydrazide see (21).]

$\bar{\text{C}}$  (1 pt.) in boilg.  $\text{AcOH}$  (6 pts.) treated with *n*-aniline (1 pt.) gives (82% yield (1)) 4,5-dichlorophthalanil (*N*-phenyl-4,5-dichlorophthalimido) [Beil. XXI-1-(301)], cryst. from  $\text{AcOH}$ , m.p. 212.5–213° cor. (1).

$\bar{\text{C}}$  on saponification with standard alkali (Sap. Eq. = 108.5), followed by acidification, yields 4,5-dichlorophthalic acid (3:4890) q.v

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 (21) Drew, Pearman, *J. Chem. Soc.* 1937, 32

3:4835 HEXACHLOROETHANE  
(Perchloroethane)



Beil. I - 87  
 I<sub>1</sub>-(26)  
 I<sub>2</sub>-(58)

M.P.

189° s.t.	(1)
187-188°	{74} (115)
187.71-188.75° cor., s.t.	(7)
187° s.t.	(2) (3)
187°	(4) (5) (6) (63) (64)
180.85-187.4° cor., s.t.	(7)
180.8°	(8)
180-187°	(9) (133)
186°	(10) (75)
185-186°	(11)
185°	(12) (13) (14) (132)
183-184° s.t.	(15)
183.0-184.0°	(16)
181° s.t.	(17)

B.P.

185.5° at 776.7 mm.	(7)
185° at 760 mm.	(18)

White cryst. with camphoraceous odor which readily sublime without melting. — Cryst. from alc., ether,  $\text{CHCl}_3$  or  $\text{CS}_2$ . —  $\bar{C}$  is trimorphous: below about 46° cryst.  $\bar{C}$  is orthorhombic, in range 46-71° cryst.  $\bar{C}$  is triclinic; about 71° cryst.  $\bar{C}$  is cubic at these transition temps. volume alterations occur which have sometimes (5) been mistaken for m.p.'s. — [For details on trimorphism and these transitions see (19) (8) (20) (21) (25) (26); for influence of high press. see (22) — For crystallographic data see (20) (23) (24); for X-ray crystallog. data see (27) (28)]

$\bar{C}$  is almost abs. insol. aq. and vice versa at ord. temp. (29); for patents on drying of  $\bar{C}$  see (30) (31) — [For studies of vap. press. of  $\bar{C}$  at various temps. see (13) (1) (7) (32). — For prevention of "caking" of cryst.  $\bar{C}$  by addn. of 1-10% paraformaldehyde see (33)]

Cryoscopic const. of  $\bar{C}$ , i.e., f.p. lowering per mole solute in 100 g.  $\bar{C}$ , is 5.6° (34). [For thermal anal. of binary systems of  $\bar{C}$  with naphthalene (1:7200) (8) (34), with phenanthrene (1:7210) (34), or with anthracene (1:7235) (31) see indic. refs.]

# USES OF $\bar{C}$

$\bar{C}$  finds many uses in industry, some based on its physical characteristics and some on its chem. behavior. — [I.g., for use of  $\bar{C}$  as solvent for prepn. of solid solns. of  $\text{I}_2$  for use in place of usual tincture see (35); for use of  $\bar{C}$  as means for temporary marking of cloth removable at will by heat (sublimation) see (36)]

[For use of  $\bar{C}$  as addition agent to  $CCl_4$  fire extinguishers see (37); as component of certain types of explosives (e.g., 75% nitrostarch + 20%  $\bar{C}$  + 5%  $NaNO_3$ ) see (38); for use of  $\bar{C}$  as mothproofing agent see (39) (40) (41) (42); for use of  $\bar{C}$  as insecticide and/or fungicide see (43) (44); for use of  $\bar{C}$  together with  $CS_2$  (45) or rotenone (46) as insecticides see indic. refs.]

$\bar{C}$  is an important component of "HC" smoke candles or grenades used for the production of screening clouds or smokes; a mixture of  $\bar{C}$  with powdered metal (usually Zn) once started undergoes vigorous decomposition yielding  $ZnCl_2 + C$ ; other materials are usually added to ignite the mixture and to modify the character of the resultant smoke; for further details see (47) (48) (49). — [For use of this type of reactn. in prepn. of activated carbon see (153)]

### PHYSIOLOGICAL ASPECTS OF $\bar{C}$

[For studies of toxicity of  $\bar{C}$  and its ability to penetrate skin see (50) (51) (52) cf. (160); for studies of  $\bar{C}$  as anthelmintic see (53) (54); for study of antiseptic power of  $\bar{C}$  see (55).]

### DETERMINATION OF $\bar{C}$

For detn. of  $\bar{C}$  by reactn. with Na + ethanolamine in dioxane followed by detn. of resultant chloride ion see (161).

### PREPARATION (OR FORMATION) OF $\bar{C}$

$\bar{C}$  is a by-product of the tech. prepn. of  $CCl_4$  (5:5100) from  $CS_2 + Cl_2$  (56), of prepn. of  $CHCl_3$  (3:5050) and of  $CH_2Cl_2$  (3:5020) (57), and is found (12) (together with other by-products) in the high-boilg. fractn. ("Tri-Nachlauf") from the prepn. of trichloroethylene (3:5170) from acetylene tetrachloride (3:5750). — For quick prepn. of  $\bar{C}$  from  $CCl_4$  (3:5100) refluxed with Al powder (80% yield (14)) or with Al/Hg (65% yield (58)) cf. (96) see indic. refs.; for prepn. of  $\bar{C}$  from ethylene with  $Cl_2$  over activated carbon at 300–350° (90% yield) see (59). — For many other methods of preparation, manufacture, or formation see below.

From various polychloroethanes. From 1,2-dichloroethane (ethylene dichloride) (3:5180). [For prepn. of  $\bar{C}$  from ethylene dichloride in vapor phase with  $Cl_2 + cat.$  (60) (61) or with  $Cl_2$  under press. (62) see indic. refs.; note that ethylene dichloride in liq. phase with  $Cl_2$  gives mainly (61) 1,1,2-trichloroethane (3:5085). — Note also that 1,2-dibromoethane (ethylene dihydride) refluxed with  $AlCl_3$  while treated with  $Cl_2$  (63) gives  $\bar{C}$ .]

From 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). [For formn. of  $\bar{C}$  together with other prods. from acetylene tetrachloride over pumice at 700° (64), or with anhydr.  $FeCl_3$  on hgt. in s.t. (65), or with  $Cl_2$  (66) in u.v. light at 50–60° (67) or X-radiation (68), or with  $Cl_2$  over activated carbon at 300–400° (69) (70) or at 60–70° (71), or with  $Cl_2$  in pres. of  $AlCl_3$  at 20–100° (71) or at 120° under reflux (80% yield (72)), or with  $Cl_2$  in pres. of Fe at 20–80° (71), or with  $Cl_2$  in  $CCl_4$  soln. (73), or even with aq. bleaching powder (71), see indic. refs. — (Note also that acetylene tetrabromide with  $AlCl_3 + Cl_2$  under reflux yields (63)  $\bar{C}$ ).]

From pentachloroethane (3:5880). [For formn. of  $\bar{C}$  together with other prods. from pentachloroethane with dry  $Cl_2 + AlCl_3$  or with carbon at 300–400° (70), or with  $Cl_2$  in u.v. exc. 10 hrs. (16), see indic. refs. — (Note also that ShC for 2 hrs. gives (75)  $\bar{C}$ ).]

From various  $\bar{C}$  (3:5170). [For formn. of  $\bar{C}$  over

pumice at 700° (64), or with anhydrous  $\text{FeCl}_3$  on htg. in s.t. (65), or with  $\text{Cl}_2$  over act. carbon at 60–70° (98% yield (70)), see indic. refs.]

*From tetrachloroethylene (3:5460).* [For prepn. and/or formn. of  $\bar{\text{C}}$  from tetrachloroethylene with  $\text{Cl}_2$  (162) (76) (77) in direct sunlight (78) cf. (79) (80) (106) or in pres. of suitable cat. in dark at 80–100° (81), or in  $\text{CCl}_4$  soln. at 22° (82) cf. (73) or in vapor phase at 40° and low press. in light and absence of oxygen (33) see indic. refs. (note that tetrachloroethylene (3:5460) with  $\text{Cl}_2$  + light in presence of  $\text{O}_2$  undergoes photo-oxidation to trichloroacetyl chloride (3:5420)).] — For formn. of  $\bar{\text{C}}$  from tetrachloroethylene with  $\text{SO}_2\text{Cl}_2$  in pres. of dibenzoyl peroxide (84), or in small amt. with dibenzoyl peroxide alone (85), or with chlorine monoxide in  $\text{CCl}_4$  at –20° (86), see indic. refs.] See also below under formn. of  $\bar{\text{C}}$  from acetylene.

*From dichloroacetylene (3:5010).* [For formn. of  $\bar{\text{C}}$  from dichloroacetylene with  $\text{Cl}_2$  in  $\text{CCl}_4$  soln. see (2).]

*From various polychloromethanes. From trichloromethane (chloroform) (3:5050).* [For formn. of  $\bar{\text{C}}$  together with other prods. from  $\text{CHCl}_3$  by pyrolysis at 425° (87), in electric arc (6), by actn. of radium radiation (88), or by actn. of  $\text{NCl}_3$  in sunlight (89) see indic. refs.]

*From carbon tetrachloride (3:5100).* [For formn. of  $\bar{\text{C}}$  together with other prods. from  $\text{CCl}_4$  by pyrolysis at 600–1500° (90) cf. (91) (76), by actn. of electric arc (6), dark elec. discharge (92), or radium radiation (88), with hydrogen at 600–650° (93), or with hydrogen over reduced Ni at 270° (94), or from  $\text{CCl}_4$  in nitrogen over  $\text{GeO}_2$  at 500–865° (95), see indic. refs.]

[For prepn. of  $\bar{\text{C}}$  from  $\text{CCl}_4$  (3:5100) by refluxing with Al powder (80% yield (14)), Al/Hg (65% yield (38)), or Al +  $\text{AlCl}_3$  (96), or by htg. with Cu powder in s.t. at 120° (97), amorphous As in s.t. at 160° (98), or molecular Ag in s.t. at 200° (99), see indic. refs.]

*From various hydrocarbons. From methane.* [For formn. of  $\bar{\text{C}}$  together with other prods. from  $\text{CH}_4$  +  $\text{Cl}_2$  in silent elec. discharge see (100).]

*From ethane.* [For formn. of  $\bar{\text{C}}$  together with other prods. from ethane with  $\text{Cl}_2$  in pres. of activated carbon or other cat. at elev. temp. see (101) (102) (103).]

*From ethylene.* [For formn. of  $\bar{\text{C}}$  together with other prods. from ethylene with  $\text{Cl}_2$  over act. carbon at 120–125° (104) or at 300–350° (90% yield (50)) cf. (101) (105).]

*From acetylene.* [For formn. of  $\bar{\text{C}}$  together with other prods. from acetylene with  $\text{Cl}_2$  at 650–1000° as directed (106) or at 700–950° as directed (107), with  $\text{Cl}_2$  in an inert gas such as  $\text{N}_2$  or  $\text{HCl}$  over act. carbon at elev. temp. (108), or with  $\text{S}_2\text{Cl}_2$  in pres. of 1–2% reduced iron (109) (110) see indic. refs. — (Note that by this mode of procedure acetylene tetrachloride (see this heading above) is a probable intermediate.)]

*From miscellaneous sources.*  $\bar{\text{C}}$  has been observed as one of the products of decomposition of many different types of compounds contg. the — $\text{CCl}_3$  group [For example, for formn. of  $\bar{\text{C}}$  (together with other prods.) from iodotrichloromethane on distn. (111), from bromotrichloromethane in ultraviolet light (112), from trichloroacetyl chloride (3:5420) at 600° (113), from trichloroacetyl bromide in s.t. at 400° (113), from trichloroacetyl iodide on distn. at ord. press. (113), from nitrosotrichloromethane with  $\text{O}_2$  at 120° (114), or from nitrotrichloromethane (chloropierin) with  $\text{HCl}$  gas over pumice at 400° (1) see indic. refs. — For formn. of  $\bar{\text{C}}$  together with other prods. from trichloroacetaldehyde (chloral) (3:5210) with  $\text{Cl}_2$ ,  $\text{Br}_2$ , or  $\text{I}_2$  in pres. of  $\text{AlCl}_3$  (115), from trichloroacetic acid (3:1150) by pyrolysis over  $\text{TiO}_2$ , kaolin, or carbon (116), from K trichloroacetate by electrolysis of its soln. in aq. KOAc (15), from ferric trichloroacetate in aq. soln. in light (117) (118) (110), from pentachlorodimethyl ether on htg. with aq. (120), or from trichloromethyl benzoate on htg. (121) see indic. refs.]

The formn. of  $\bar{\text{C}}$  has also been observed in connection with certain acid chlorides [e.g.,

for formn. of  $\bar{C}$  from acetyl chloride (3:7065) with excess  $PCl_5$  in s.t. nt  $180^\circ$  (122), from pentachloropropionyl chloride (3:0470) with  $AlCl_3$  on warming (123), from dichloromaleyl (di)chloride (3:6197) with  $PCl_5$  nt  $230^\circ$  for 6 hrs. (124), or from pentachloroethyl chloroformate with  $AlCl_3$  at  $100^\circ$  (125) see indic. refs.]

[For formn. of  $\bar{C}$  from various alkanes with  $SbCl_5 + I_2$  (126), from a mixt. of dichloropropanes or from hexachlorobutadiene (3:6425) with  $Cl_2$  at  $400^\circ$  and 30 atm. (127), from an electric arc between carbon electrodes in  $Cl_2$  (128), from *n*-propyl chloride (3:7040) or isobutyl chloride (3:7135) with excess  $ICl_3$  in s.t. nt  $200^\circ$  (129), from  $CaC_2$  with gaseous or liq.  $Cl_2$  at  $20^\circ$  under press. (10), from various iodochlorides of ethylene on warming (9), from lignin on oilg with  $SbCl_5 + I_2$  (130), from humic acid with  $KClO_3 + HCl$  (131), from  $\beta, \beta'$ -dichlorodiethyl sulfide ("mustard gas") with dry  $Cl_2$  at  $100^\circ$  (132), or from  $\alpha, \alpha, \beta, \beta, \beta', \beta'$ -hexachlorodiethyl sulfide or  $\alpha, \alpha, \beta, \beta, \beta', \beta'$ -heptachlorodiethyl sulfide with  $Cl_2$  in cold (133) see indic. refs.]

### CHEMICAL BEHAVIOR OF $\bar{C}$

**Pyrolysis.** [ $\bar{C}$  passed over porcelain in hot tube gives (78) tetrachloroethylene (3:5460);  $\bar{C}$  (in stream of air) pyrolyzed nt  $550$ – $600^\circ$  gives (57) tetrachloroethylene (3:5460) +  $CCl_4$  (3:5100) in conversions of substantially 100%. — Note also that  $\bar{C}$  with  $SbCl_5$  above  $450^\circ$  yields almost exclusively (126)  $CCl_4$  (3:5100).]

**Reduction.**  $\bar{C}$  with granulated Zn in boilg. alc. (134), with Zn + dil.  $H_2SO_4$  nt room temp. for several days (100% yield (135)) (136) (76), with Zn + aq. above  $80^\circ$  (137), with  $H_2$  over Ni nt  $270^\circ$  (138), or with alc. KSH (139) loses 2 chlorine atoms giving tetrachloroethylene (3:5460) [for other, less direct conversions of  $\bar{C}$  to tetrachloroethylene see latter under preparation; also below.]]

**Oxidation.**  $\bar{C}$  is oxidized only with considerable difficulty [e.g., for behavior of  $\bar{C}$  over hot CuO see (140); for detn. of chlorine in  $\bar{C}$  by cat. oxidn. over  $Fe_2O_3$  (low results) see (141);  $\bar{C}$  with  $CrO_3/H_2SO_4$  is incompletely oxidized (142);  $\bar{C}$  with  $SO_3$  in s.t. nt  $150^\circ$  (143) cf. (144) yields trichloroacetyl chloride +  $S_2O_5Cl_2$ .]

**Partial replacement of chlorine by fluorine.** [ $\bar{C}$  with  $F_2$  gas over Cu gauze cat. st  $125^\circ$  (145), or with  $SbF_3Cl_2$  htd. under press. (146) (147) (148), or with  $SbF_3 + Cl_2 + SbCl_5$  as directed (149) yields 1,1,2,2-tetrachloro-1,2-difluoromethane, m.p.  $24$ – $25^\circ$ , h.p.  $92^\circ$ , accompanied by numerous other partially fluorinated prods.]]

**Behavior with alkalis.** [ $\bar{C}$  with solid KOH in s.t. nt  $210$ – $220^\circ$  for several days yields (150) KCl + potassium oxalate;  $\bar{C}$  with alc. KOH in s.t. at  $100^\circ$  for a week yields (151) the same prods. accompanied by ethylene and hydrogen;  $\bar{C}$  with *N*/10 abs. EtOH/NaOH at  $25^\circ$  (17), with alc.-free NaOEt in ether under press. htd. to  $140^\circ$  (152), yields tetrachloroethylene (3:5460) (for study of kinetics see (17)).]

**Behavior with metals.** [ $\bar{C}$  with alk. or alk.-earth metals is (like many other polychloro compounds) subject to explosion by mechanical shock; for study of sensitivity of  $\bar{C}$  with Li, Na, K, Mg, Ca, Sr, Ba, Al, or Ti see (154). —  $\bar{C}$  with "molecular" Ag at  $280^\circ$  loses 2 atoms of chlorine yielding (99) tetrachloroethylene (3:5460).]

**Behavior with organometallic compounds.** [For behavior of  $\bar{C}$  with  $RMgX$  compds. see (155) (166);  $\bar{C}$  does not (11) react with Hg di-(*p*-tolyl).]

**Behavior with  $NH_3$  or organic bases.** [ $\bar{C}$  with  $NH_3$  at  $700$ – $800^\circ$  gives up its halogen quant. (157) yielding  $NH_4Cl$ . —  $\bar{C}$  with excess phenylhydrazine in xylene soln. on stdg. or on warming is reduced to tetrachloroethylene (3:5460),  $HCl$ ,  $C_6H_6$ , and  $N_2$  also being formed (158) (note that analogous reactns. are also shown by 1,1,2,2-tetrachloroethane (3:5750) and by pentachloroethane (3:5880)). — For kinetics of reactn. of  $\bar{C}$  with pyridine or piperidine see (159).]

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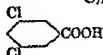
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## 3:4840 3,5-DICHLOROBENZOIC ACID

 $C_7H_4O_2Cl_2$ 

Beil. IX - 344

IX<sub>1</sub>-(141)

M.P. 188° (1) (2) (3) (4) (5)

184-185° (6)

182.5-183° (7) (11)

182-182.5° (8)

Ndls from alc. — Sublimes (10). — Very eas. sol. alc., spar. sol. aq. or lgr.

[For prepn from 3,5-dichlorotoluene (3:6310) by oxidn. with dil.  $HNO_3$  at 150-170° see (8) (7); from 3,5-dichlorobenzaldehyde (3:1475) by oxidn. with  $KMnO_4$  (74% yield) see (3); from 3,5-dichlorobiphenyl (3:0360) by oxidn. with  $CrO_3 + AcOH$  see (9); for prepn. from 3,5-diaminobenzoic ac. via diazo reactn. see (1), from 4-amino-3,5-dichlorobenzoic ac. via diazo reactn. see (2); from 3,5-dichloroaniline via conv. to acid hydrolysis of the nitrile see (10), for prepn. from 5-nitro-3-sulfobenzoic acid via  $PCl_5$  and subsequent boilg. with alk. see (11).]

$\bar{C}$  added to 8 pts. fuming  $HNO_3$  ( $D = 1.48$ ), stood 2-3 hrs. at 70°, cooled, ppts. 75% yield 2-nitro-3,5-dichlorobenzoic ac., ndls. from dil. alc., m.p. 194° cor. (5). [This prod. depresses m.p. of  $\bar{C}$  (5).]

$\bar{C}$  with  $PCl_5$  yields (12) 3,5-dichlorobenzoyl chloride, b.p. 135-137° at 25 mm. (12).

— Methyl 3,5-dichlorobenzoate: m.p. 58° (13).

— Ethyl 3,5-dichlorobenzoate: m.p. unrecorded. [For study of velocity of hydrolysis see (14).]

— 3,5-Dichlorobenzamide: unrecorded.

— 3,5-Dichlorobenzanilide: ndls. from dil. alc., m.p. 145° (15).

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## 3:4845 6-CHLORONAPHTHOIC ACID-1

 $C_{11}H_7O_2Cl$ 

Beil. S.N. 951



M.P. 189° cor. (4)

188-189° (1) (2)

Cryst. from  $C_6H_6$  or 95% alc.

[For formn. of  $\bar{C}$  from furoic acid (1:0475) + chlorobenzene (3:7903) +  $AlCl_3$  (18% yield (2)) (3) or from methyl furoate (1:3452) + chlorobenzene (3:7903) +  $AlCl_3$  (yield 39% (1)) see indic. refs.]

$\bar{C}$  on decarboxylation by htg. in quinoline nt 225° in pres. of copper chromite cat. for 4 hrs. yields (2) 2-chloronaphthalene (3:1285), m.p. 58-59° (2).

— Methyl 6-chloro-1-naphthoate: b.p. 165-170° at 2 mm. (1). [From methyl furoate (1:3452) + chlorobenzene (3:7903) +  $AlCl_3$  (15% yield (1)).]

— Ethyl 6-chloro-1-naphthoate: unreported.

① *p*-Bromophenacyl 6-chloro-1-naphthoate: m.p. 142-143° cor. (4).

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### 3:4850 PENTACHLOROPHENOL



$C_6HOC_5$

Beil. VI - 194  
VI<sub>1</sub>-(104)  
VI<sub>2</sub>-(182)

M.P. 190.2° (1)

190-191° (2) (3) (4)

189° (5)

186-187° (8) (9)

(10) (15)

B.P. 309-310° at 754.3 mm. sl. dec. (7)

195° at 16 mm.

(3)

Cryst. from alc. as monohydrate,  $\bar{C} \cdot H_2O$ , m.p. 174°; anhydrous ndls. from  $C_6H_6$ ; sublimes in long ndls. — Very insol. aq. (17), very eas. sol. alc., ether; mod. sol.  $C_6H_6$ ; spar. sol. cold lgr.; for quant. data on solubility in 15 solvents at 7 temps. from 0° to 60° see (1) (17). — Odor pronounced only on htg.; dust of  $\bar{C}$  causes sneezing. — Slightly volatile with steam.

[For general review see (1), for use as wood preservative see (17) (19); for studies on toxicity see (20) (21); for fate of  $\bar{C}$  in organism see (22).]

[For prepn. see Beil. VI-194, VI<sub>1</sub>-(104); for comml. prepn. from hexachlorobenzene (3:4939) + NaOH + MeOH see (12) cf. (23); from chlorination of phenol or polychlorophenols in pres. of  $AlCl_3$  see (13), from "hexachlorophenol" (3:3180) by reduction with  $SO_2$  in alc. see (18).]

$\bar{C}$  is acidic and in alc. soln. titrates quant. using thymol-blue (Neut. Eq. = 266.5) (1). [For dissociation const. see (2).] —  $\bar{C}$  is insol. in  $NH_4OH$  (1) but slowly dis. in cold  $Na_2CO_3$  soln. (8) —  $\bar{C}$  in alk. soln. does not couple with diazonium salts. [For spectrophotometric detn. see (11).]

Salts. See Beil. VI-194.  $Na\bar{A}$ , ndls. (from acetone + lgr.), spar. sol. aq. (3),  $Na\bar{A} \cdot H_2O$ , loses aq. at 110°, sol. aq., alc., ether. [For comml. application as preservative see (1) (14).] —  $Ag\bar{A}$ , yel. ppt. turning orange on drying. — Heavy metal salts insol. aq. and often colored (1).

$\bar{C}$  in alk. shaken with  $(CH_3)_2SO_4$  (6), or  $\bar{C}$  treated with diazomethane (6), or  $\bar{C}$  htd. in MeOH with  $CH_3I$  + KOH (15), yields its methyl ether, pentachloroanisole, ndls. from alc., m.p. 108° (6), 106.5° (6).

① Pentachlorophenyl acetate: from  $\bar{C}$  on htg. with  $Ac_2O$  +  $NaOAc$  (15) or from  $\bar{C}$  in  $CS_2$  +  $AcCl$  +  $AlCl_3$  (16); ndls. from alc., m.p. 149.5-150.5° (16), 147-148° (15). [This prod. is very resistant to saponification (16).]

③ Pentachlorophenyl benzoate: from  $\bar{C}$  +  $BzCl$  by warming in pyridine (3); ndls. from alc., m.p. 164-165° (3), 150-160° (15), 159° (19). [Very resistant to saponification (16)]

(1) (2) Tiessens, *Rec. trav. chim.* 14020 (1904). (4) Fels, *Z. Krist.* 32, 369 (5). (6) Pollak, Gebauer-Fulnegg, *Monatsh.* 20, 545 (1890). (8) Merz, Werth, *Ber.* 5, 1. (10) Brazier, McCombie, *J. Chem. Soc.*

(11) Smith, Livak, 32, 2548 (1938). (12) 4312; *C.A.* 32, 339; *Cent* 1939, (3) 13, 342-343 (13). (14) Britton, Alquist (to Dow Chem Co.), US 2,176,417, Oct. 17, 1939, *C.A.* 34, 1038 (1940). (19) Hatfield, *Proc. Am. Wood Preserving Assoc.* 1944, 4765, *C.A.* 39, 2631 (1945). (20) Goodnight, *Ind. Eng. Chem.* 34, 868-872 (1942)

(21) Deichmann, Machle, Kitamiller, Thomas, *J. Pharmacol.* 76, 104-117 (1942); *C.A.* 37, 461 (1943). (22) Machle, Deichmann, Thomas, *J. Ind. Hyg. Toxicol.* 25, 192-194 (1943). (23) Troitskii, Voronina, *Org. Chem. Ind. (U.S.S.R.)* 7, 240-241 (1940); *C.A.* 35, 3989 (1941).

3:4853 CHLOROFUMARIC ACID  $Cl-C-COOH$   $C_4H_3O_4Cl$  Beil. II - 744  
 $HOOC-C-H$  II<sub>1</sub>-(302)  
II<sub>2</sub>-(6410)

M.P. 193°	(1)
192°	(2) (3) (4)
191.5-192.5° cor.	(5)
191.5°	(6)
191-192°	(22)
191°	(8) (10) (19)
199-191°	(7) (12)
189°	(11)
188-189°	(14)

[See also chloromaleic acid (3:3432).]

TbIs from AcOH —  $\bar{C}$  is very eas. sol. aq, alc. or ether; spar. sol.  $C_6H_6$  or lgr. —  $\bar{C}$  sublimes without forming anhydride

[For prepn of  $\bar{C}$  from chloromaleic acid (3:3432) by repeated evapn. with conc. HCl see (5) (2); from *d,l*- $\alpha,\alpha'$ -dichlorosuccinic acid (3:4711) on boilg. with aq (7), or with aq. KOH (8) (9) or aq acid (9) see indic refs; from *meso*- $\alpha,\alpha'$ -dichlorosuccinic acid (3:4930) with aq KOH at 0° see (7) (8) (9) (note that from this source action of acid yields (9) both  $\bar{C}$  and chloromaleic acid (3:3432)), from diethyl *d,l*- $\alpha,\alpha'$ -dichlorosuccinate (3:9578) on hydrolysis with boilg. 30%  $H_2SO_4$  see (1); from diethyl chlorofumarate (3:6864) by evapn. with 1:1 HCl see (6); from chlorofumaro(di)nitrile (b.p. 172° at 74 mm., 64.0-64.2° at 10 mm.,  $D_4^{20} = 1.2499$ ,  $n_D^{20} = 1.49571$  (22)), by hydrol. see (22)]

[For formn of  $\bar{C}$  from diethyl oxaloacetate [Beil. III-782, III<sub>1</sub>-(273), III<sub>2</sub>-(479)] by actn. of  $PCl_5$  followed by alc. KOH see (11); from acetylenedicarboxylic acid [Beil. II-801, II<sub>1</sub>-(317), II<sub>2</sub>-(670)] with conc. HCl on stdg. 19 days at room temp. see (12) cf. (13); from 3-chlorofuroic acid [Beil. XVIII-282] on oxidn with dil  $HNO_3$  or from 3,5-dichlorofuroic acid [Beil. XVIII-283] or 4,5-dichlorofuroic acid [Beil. XVIII-283] on oxidn. with  $Br_2$ /aq. see (14).]

$\bar{C}$  on gentle boilg. largely decomposes into  $CO + CO_2 + HCl$  (5); but  $\bar{C}$  on vigorous boilg. splits off aq. and isomerizes (or vice versa) yielding (5) chloromaleic anhydride (3:0280). —  $\bar{C}$  with  $P_2O_5$  (6) (15), or with  $POCl_3$  (16) or with  $AcCl$  (5), gives on distn. chloromaleic anhydride (3:0280). —  $\bar{C}$  (1 mole) with chlorofumaryl (di)chloride (3:6105) (1 mole) at 125° for 1 hr. also yields (17) chloromaleic anhydride (3:0280).

[ $\bar{C}$  (as  $K_2\bar{A}$ ) in aq. soln. with  $Na/Hg$  is dehalogenated and reduced yielding (18) succinic acid (1:0530).]

$\bar{C}$  readily reduces aq.  $KMnO_4$ .

[ $\bar{C}$  in aq. soln. on protracted treatment with  $Cl_2$  gives (19)  $\beta,\beta,\beta$ -trichloro- $\alpha,\alpha$ -dihydroxypropionic acid ("trichloropyruvic acid hydrate") [Beil. III-623, III<sub>2</sub>-(408)], adls. from  $CHCl_3$ , m.p. 102° (19). —  $\bar{C}$  does not (5) add  $Br_2$  even at 100° (dif. from chloromaleic acid (3:3432)).]

$\bar{C}$  behaves normally as a dibasic acid: e.g., titration with standard dil. aq. alk. gives Neut. Eq. 75.3; for study of electrometric titration see (2).

[Salt.  $(NH_4)_2\bar{A}$ , cas. sol. aq. (5), but spar. sol.  $MeOH$ ,  $EtOH$ , and insol. in ether, acetone,  $AcOEt$ ,  $CHCl_3$ , or  $C_6H_6$  (20) see indic. refs. —  $KH\bar{A}$ , much less sol. than corresp. prod. from chloromaleic acid, e.g., 100 g. of its satd. soln. at 15° conts. 3.843 g.  $KH\bar{A}$  (5). —  $Ag_2\bar{A}$  (10) (12). —  $Ba\bar{A} \cdot 3H_2O$ , fairly sol. aq. (10). —  $Pb\bar{A} \cdot 2H_2O$  (13).]

[ $\bar{C}$  on stdg. at ord. temp. with slight excess 0.76  $N$  aq.  $KOH$  gives chlorine ion about 40 times as fast (12) as the isomeric chloromaleic acid (3:3432).]

The acid (di)chloride corresp. to  $\bar{C}$ , viz., chlorofumaryl (di)chloride (3:6105), has been reported only by indirect means.

— Dimethyl chlorofumarate: oil (see 3:6582).

— Diethyl chlorofumarate: oil (see 3:6864).

① *bis*-(*p*-Nitrobenzyl) chlorofumarate: m.p. 138.5° (21). [From  $Na_2\bar{A}$  with *p*-nitrobenzyl bromide in 63% alc. refluxed 2 hrs. (21).]

— Chloromaleanil [*N*-phenyl-chloromaleinimide]: adls. from boilg. alc., m.p. 170° (17). [From aniline salt of  $\bar{C}$  on litg. for a few minutes at 170°–180°; note that during the process isomerization occurs and therefore that the prod. is the same as similarly obt'd. from chloromaleic acid (3:3432) q.v.]

② Chlorofumaro-*bis*-(*p*-chloroanilide): pale yel. ndls. from alc., m.p. 223° (17). [From chlorofumaryl (di)chloride (3:6105) with *p*-chloroaniline (4 moles) in dry ether; note that crude prod. is also accompanied by a little *N*-(*p*-chlorophenyl)-chloromaleinimide, m.p. 175° (17).]

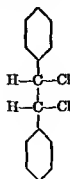
③ Chlorofumaro-*bis*-(*p*-bromoanilide): faintly yel. ndls. from boilg. alc., m.p. 236° (17). [From chlorofumaryl (di)chloride (3:6105) with *p*-bromoaniline (4 moles) in dry ether; note that crude prod. is also accompanied by a little *N*-(*p*-bromophenyl)-chloromaleinimide, m.p. 190° (17).]

3:4853 (1) Patterson, Todd, *J. Chem. Soc.* 1629, 1769, 1770. (2) Ashton, Partington, *Trans. Faraday Soc.* 36, 602, 605–606, 608 (1934). (3) Langseth, *Z. physik. Chem.* 118, 64 (1925). (4) Stelling, *Z. physik. Chem.* B-24, 416, 424 (1934). (5) Perkin, *J. Chem. Soc.* 53, 697–700, 703–705 (1888). (6) von Auwers, Harren, *Ber.* 62, 1685–1687 (1929). (7) Michael, Tisserand, *J. prakt. Chem.* (2) 46, 393–395 (1862). (8) Robinson, Lewis, *J. Chem. Soc.* 1933, 1260. (9) Holmberg, *Arkiv Kemi, Mineral., Geol.* 8, No. 2, 33 (1920); *Cent.* 1621, 1830; *C.A.* 16, 2116 (1922). (10) Kauder, *J. prakt. Chem.* (2) 31, 29–32 (1885).

(11) Nef, *Ann.* 276, 223–226 (1893). (12) Michael, *J. prakt. Chem.* (2) 52, 306–308, 321–322 (1895). (13) Bandrowski, *Ber.* 15, 2695 (1882). (14) Hill, Jackson, *Am. Chem. J.* 12, 36, 50, 115 (1890). (15) Walden, *Ber.* 36, 2885–2886 (1897). (16) Thomas-Mamert, *Bull. soc. chim.* (3) 13, 847 (1895). (17) Chattaway, Parkes, *J. Chem. Soc.* 125, 466 (1924). (18) Perkin, *Ann.* 129, 373–374 (1864). (19) Büchner, *Ber.* 26, 656–657 (1863). (20) McMaster, Magill, *J. Am. Chem. Soc.* 38, 1802–1803 (1916).

{21} Lyons, Reid, *J. Am. Chem. Soc.* **39**, 1733 (1917). {22} Mommaerts, *Bull. classe sci., Acad. roy. Belg.* (5) **27**, 579-597 (1941); *Cent.* **1943**, I 615-616; *C.A.* **38**, 3621 (1944).

3:4854 *meso*-1,2-DICHLORO-1,2-DIPHENYLETHANE  
(*meso*- $\alpha,\alpha'$ -Dichlorobiphenyl;  
"  $\alpha$  "stilbene dichloride)


 $C_{14}H_{12}Cl_2$ 

Beil. V - 609  
V<sub>1</sub>-(281)  
V<sub>2</sub>-(597)

M.P. [194.5-195.5° cor. (1) (15)]  
193-194° (25)  
193° (2) (6)  
192.4-193.4° cor. (3)  
192-193° (5) (19) (22)  
192° (4) (5) (6)  
191-193° (7) (17)  
191-192° (16), u.c. (15)  
190-192° (21)  
191° (9) (10)  
190.5-101° (11)  
190° (12) (13)  
189-199° (14)  
188-189° (20)

[See also the isomeric *d,l* or "  $\beta$  "stilbene dichloride (3:2570).]

Colorless ndls. from alc., AcOH,  $C_6H_6$ , toluene, or lgr. — Spar. sol. hot alc., eas. sol. hot toluene. — Sublimes.

## PREPARATION OF $\bar{C}$

### FROM BINUCLEAR INITIAL MATERIALS

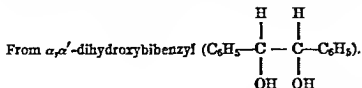
From stilbene (*trans*-1,2-diphenylethylene). [For prepn. of  $\bar{C}$  from 1,2-diphenylethylene (stilbene) (1:7250) with  $Cl_2$  in  $CHCl_3$  (8) (16), with  $Cl_2$  in ether in sunlight (17) (some "  $\beta$  "stilbene dichloride (3:2570) is also formed), with  $Cl_2$  in ethane soln. (note low temp.) in sunlight (gives 34.4% yield  $\bar{C}$  + 48.7% yield diastereomer (3:2570) (15)) see indic. refs.; with  $PCl_5$  (2 moles) in  $CHCl_3$  soln. (6) or with  $PCl_5$  in  $POCl_3$  in s.t. at 170° (2) see indic. refs.; with  $SO_2Cl_2$  in presence of peroxides at room temp. (yield of crude mixt. is 100%; sepn. of isomers gives 45%  $\bar{C}$  + 33% diastereomer (3:2570) (7)), with nitryl chloride ( $ClNO_2$ ) in ether (57% yield (18)), see indic. refs.]

From isostilbene (*cis*-1,2-diphenylethylene). [For prepn. of  $\bar{C}$  from isostilbene with  $PCl_5$  in  $C_6H_6$  stood 2 days at room temp. see (6).]

From bibenzyl. [For formn. of  $\bar{C}$  from bibenzyl (1:7149) with chromyl chloride ( $CrO_2Cl_2$ ) in  $CS_2$  (other prods. are also formed) see (19).]

From  $\alpha,\alpha'$ -dibromobiphenyl (stilbene dibromide). [For formn. of  $\bar{C}$  from the higher-melting diastereomer (m p. 236°) of stilbene dibromide [Beil. V-602, V<sub>1</sub>-(282), V<sub>2</sub>-(508)] with  $SnCl_4$  in  $C_6H_6$  on refluxing  $\frac{1}{2}$  hr. (5) (note that at ord. temp. replacement is only

partial and yields (5) only stilbene chlorobromide, m.p. 225°) or with  $\text{HgCl}_2$  in acetone/ $\text{CHCl}_3$  refluxed 11 hrs. (poor yield (11)) see indic. refs.]



From *meso*-hydrobenzoin. [For prepn. of  $\bar{\text{C}}$  from *meso*-hydrobenzoin [Beil. VI-1003, VI-1-(490)] with  $\text{PCl}_5$  (2 moles) (20) cf. (15) (yield 43%  $\bar{\text{C}}$  + 22% diastereomer (3:2570) (8) (16)), with  $\text{PCl}_5$  (8) (16), or with  $\text{SOCl}_2$  in  $\text{C}_6\text{H}_6$  + pyridine (100% yield (10)) (13) see indic. refs.]

From *d,l*-hydrobenzoin (*isohydrobenzoin*). [For prepn. of  $\bar{\text{C}}$  from *isohydrobenzoin* [Beil. VI-1004, VI-1-(490)] with  $\text{PCl}_5$  (27-32%  $\bar{\text{C}}$  + much resin (8)) (16) (20) or with  $\text{PCl}_5$  (5) (16) see indic. refs.; note, also, that *l*-isohydrobenzoin with  $\text{PCl}_5$  in  $\text{CHCl}_3$  refluxed 2 hrs. gives (45% yield (1))  $\bar{\text{C}}$ .]

From  $\alpha$ -chloro- $\alpha'$ -hydroxybibenzyl. [For formn. of  $\bar{\text{C}}$  from  $\alpha$ -chloro- $\alpha'$ -hydroxybibenzyl (m.p. 77°, corresp. *p*-nitrobenzoate, m.p. 103-104° (3)) with  $\text{SOCl}_2$  in  $\text{CHCl}_3$  see (3); note that by this method  $\bar{\text{C}}$  is formed exclusively.]

From  $\alpha$ -amino- $\alpha'$ -hydroxybibenzyl. [For prepn. of  $\bar{\text{C}}$  from *d,l*- $\alpha$ -amino- $\alpha'$ -hydroxybibenzyl with  $\text{PCl}_5$  (42% yield (21)) or with  $\text{NOCl}$  (1) see indic. refs.; note also that *d*- $\alpha$ -amino- $\alpha'$ -hydroxybibenzyl in  $\text{HCl}$  with  $\text{NOCl}$  gives (1) 13%  $\bar{\text{C}}$  + 24% of *l*-" $\beta$ "-stilbene dichloride (3:2570) while *l*- $\alpha$ -amino- $\alpha'$ -hydroxybibenzyl in  $\text{HCl}$  with  $\text{NOCl}$  gives (1) 14%  $\bar{\text{C}}$  + 17% *d*-" $\beta$ "-stilbene dichloride (3:2570).]

#### FROM MONONUCLEAR INITIAL MATERIALS

From benzal (di)chloride. [For formn. of  $\bar{\text{C}}$  from benzal (di)chloride (3:6327) by bimolecular reduction with  $\text{H}_2$  + Pd in alc. soln. (22), or with  $\text{H}_2$  + hydrazine hydrate in  $\text{MeOH/KOH}$  (20% yield (12)), or with excess conc. (2 molar)  $\text{MeMgI}$  in ether refluxed 2 hrs. (22% yield (14)), or with excess  $\text{C}_6\text{H}_5\text{MgBr}$  similarly (14), or by action of Ni on hgt. in  $\text{CO}_2$  (23), see indic. refs.]

From benzotrichloride. [For formn. of  $\bar{\text{C}}$  from benzotrichloride (3:6540) by actn. of Ni on hgt. in atm. of  $\text{CO}_2$  see (23).]

#### FROM MISCELLANEOUS INITIAL MATERIALS

[For formn. of  $\bar{\text{C}}$  from diphenylacetaldehyde [Beil. VII-438, VII-1-(234)] with  $\text{PCl}_5$  in  $\text{C}_6\text{H}_6$  under reflux 2 hrs. (41% yield) see (3).]

#### CHEMICAL BEHAVIOR OF $\bar{\text{C}}$

<sup>1</sup> Action of heat.  $\bar{\text{C}}$  on repeated hgt. above its m.p. is partially isomerized to its diastereoisomer (3:2570) as a result of which the m.p. of the sample gradually falls to about 160° but not lower (8) (16).

Reduction.  $\bar{\text{C}}$  with Zn dust +  $\text{AcOH}$  gives good yields (24) of *trans*-1,2-diphenylethylene (stilbene) (1:7250), m.p. 124°.

Hydrolysis. [No study of the direct hydrolysis of  $\bar{\text{C}}$  appears to be recorded. — However,  $\bar{\text{C}}$  with  $\text{AgOAc}$  in boilg.  $\text{AcOH}$  gives an ester which upon hydrolysis gives (60% yield (8) (16)) almost exclusively *d,l*-hydrobenzoin (*isohydrobenzoin*), accompanied by a little

hydrobenzoin; with AgOBz, however, much more of the latter results; however, see also below.]

Other reactions.  $\bar{C}$  with alc. KOH on warming under reflux (20) or in an autoclave at 180° (2) splits out 2 HCl yielding diphenylacetylene (tolane) [Beil. V-656, V<sub>1</sub>-(319), V<sub>2</sub>-(568)], m.p. 60°. —  $\bar{C}$  with pyridine in s.t. at 200° for 8 hrs. does not (17) split out HCl (dif. from the "β" stereoisomer (3-2570) q.v.)

[ $\bar{C}$  with Lil in alc. refluxed 2 hrs. is little affected but in s.t. at 200° for 3 hrs. gives (11) (presumably via halogen interchange and subsequent loss of I<sub>2</sub>) a little *trans*-1,2-diphenylethylene (stilbene) (1:7250). —  $\bar{C}$  with NaI in alc. is unchanged even at 150° in s.t.; using AcOH as solvent, however, in s.t. at 210° stilbene (1:7250) is formed (11). —  $\bar{C}$  does not (11) react with alc. NaBr.]

[ $\bar{C}$  with AgOAc (2 moles + 25% excess) in AcOH at 100° for 9 hrs. gives (25) mixts. of hydrobenzoin diacetate, m.p. 133-134°, and isohydrobenzoin diacetate, m.p. 114-116° (for m.p./compn. diagram of this pair see (25) (26)).]

3:4854 (1) Weissberger, Bach, *Ber* 64, 1095-1108 (1931). (2) Kayser, *Ann. chim.* (11) 6, 220-222 (1936). (3) Newman, Joshel, Wisc. *J. Am. Chem. Soc.* 62, 1862 (1940). (4) Reulos, *Compt. rend.* 216, 775-776 (1943). (5) Pfeiffer, Eistert, *J. prakt. Chem.* (2) 124, 174-175 (1930). (6) Bergmann, Bondi, *Ber.* 64, 1457-1458, 1468 (1931). (7) Kharasch, Brown, *J. Am. Chem. Soc.* 61, 3434 (1939). (8) Zincke, *Ann.* 193, 129-141 (1879). (9) Higashi, *Bull. Chem. Soc. Japan*, 13, 159 (1935). (10) Kitasato, Sone, *Ber.* 64, 1144 (1931).

(11) Pfeiffer, Praetorius, *J. prakt. Chem.* (2) 137, 30-31, 37-39 (1933). (12) Busch, Weber, *J. prakt. Chem.* (2) 146, 49-50 (1936). (13) Carré, Maucelère, *Compt. rend.* 192, 1563-1569 (1931). (14) Fuson, Ross, *J. Am. Chem. Soc.* 55, 720-723 (1933). (15) Weissberger, Stangenwald, *Z. physik. Chem. B-9*, 140 (1930). (16) Zincke, *Ber.* 10, 999-1004 (1877). (17) Pfeiffer, *Ber.* 45, 1816-1817 (1912). (18) Steinkopf, Kühnel, *Ber.* 75, 1327 (1942). (19) Weller, *Ber.* 32, 1054 (1899). (20) Fittig, Ammann, *Ann.* 168, 73-74, 77-78 (1873).

(21) Darapsky, Spannagel, *J. prakt. Chem.* (2) 92, 293 (1915). (22) Borsche, Heimbürger, *Ber.* 48, 457 (1915). (23) Korczynski, Reischholz, *Schmidt, Roczniki Chem.* 9, 731-740 (1920); *Cent.* 1930, I 2075, *C.A.* 24, 1858 (1930). (24) Meisenheimer, Heim, *Ann.* 356, 274 (1907). (25) Winstein, Seymour, *J. Am. Chem. Soc.* 68, 119-122 (1946). (26) Böseken, Elson, *Rec. trav. chim.* 47, 696 (1928).

3:4855 5-CHLOROBENZENETRICARBOXYLIC  $C_6H_3O_3Cl$  Beil. S.N. 1008  
ACID-1,2,4  
(5-Chlorotrimellitic acid)



M.P. 192-194° (1)

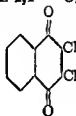
[For prepn. of  $\bar{C}$  from 5-chloro-1,2,4-trimethylbenzene (5-chloropseudocumene) [Beil. V-402] by oxidn. in aq. pyridine with KMnO<sub>4</sub> see (1).]

[ $\bar{C}$  on suitable treatment with alk. yields (1) 5-hydroxytrimellitic acid [Beil. X-580] for use as dye intermediate.]

3:4855 (1) I.G., Brit. 495,432, Dec. 8, 1938; *Cent.* 1939, I 1452; *C.A.* 33, 2913 (1939); French 839,454, April 4, 1939, *C.A.* 36, 5188 (1942).



3:4857 2,3-DICHLORONAPHTHOQUINONE-1,4  $C_{10}H_4O_2Cl_2$  Beil. VII - 729  
VII<sub>1</sub>-(386)



M.P. 196°	(1)
193°	(2) (3)
192.5° cor.	(4)
192°	(5)
190° cor.	(6)
189-192°	(7)
189-190°	(8)
189° u.c.	(9)
189°	(10) (11)
188.5° u.c.	(4)
188°	(20)
186°	(12)

Golden yellow ndls. from AcOH (contg. a little  $CrO_3$  (2)) or from alc. — Sublimes (use in purification (12)). — Insol. aq. (1 in 19,000,000 (13)), spar. sol. cold alc AcOH,  $CCl_4$ , ethyleneglycol ethyl ether, gasoline, cottonseed oil, castor oil, "Nujol" (13); quite sol. (4%) (13) in xylene or *o*-dichlorobenzene (3:6055); fairly sol. in ether,  $C_6H_6$ , acetone, or dioxane (13).

[For use of  $\bar{C}$  as agricultural and textile fungicide see impt. review article (13) cf. (37).]

[For prepn. of  $\bar{C}$  from naphthoquinone-1,4 (1:9040) in AcOH with  $Cl_2$  in pres. of  $I_2$  (yields: 90% (14), 80% (8)), from 2-chloronaphthoquinone-1,4 [Beil. VII-729] in AcOH with  $Cl_2$  (15) (16), from naphthoquinone-1,4-*N*-chloromonimide [Beil. VII-726] in AcOH with 8-10 pts. conc. HCl on warming (70% yield (11)) see indic. refs.; from naphthol-1 (1:1500) with HCl +  $KClO_3$  (6) or after preliminary sulfonation to naphthol-1-sulfonic acid-4 (Neville-Winther acid) followed by HCl +  $KClO_3$  (yields: 83% crude (4), 47% (2), 40-47% (12)) (17) (18), from 4-nitronaphthol-1 (naphthoquinone-1,4-monoxime) [Beil. VII-727, VII<sub>1</sub>-(386)] in ether with HCl gas (3), from 4-aminonaphthol-1 in AcOH with  $Cl_2$  (17), from 2,3-dichloronaphthol-1 (3:2935) in AcOH with  $CrO_3$  (19), or from 2,4-dinitrophenol (Martius Yellow) [Beil. VI-617, VI<sub>1</sub>-(303)] with HCl +  $KClO_3$  (24% yield (2)) (10) see indic. refs.]

[For formn. of  $\bar{C}$  from 1,4-dihydroxynaphthalene-3-pyridinium chloride (itself from naphthoquinone-1,4 (1:9040) + pyridine in MeOH + HCl) with  $SOCl_2$  under reflux see (7); from naphthalene (1:7200) in AcOH with  $CrO_2Cl_2$  see (20); from 1,2,3,4-tetrachloronaphthalene [Beil. V-546, V<sub>2</sub>-(446)] in AcOH with  $CrO_3$  or with conc.  $HNO_3$  in s.t. at 110° see (9); from naphthalene tetrachloride-1,2,3,4 (3:4750) with conc.  $HNO_3$  see (1); from 2,2,3,4,4-pentachloro-1-oxo-naphthalene tetrahydride [Beil. VII-370] with dil. alc. or dil. AcOH in s.t. at 120-130° see (15).]

[ $\bar{C}$  on reduction by shaking ether soln. with aq.  $SnCl_2$  (21), or with Sn + HCl (part of halogen is lost (10)), or by refluxing with HI + white P (10) gives 2,3-dichloro-1,4-dihydroxynaphthalene [Beil. VI-979], colorless scales from alc., m.p. 135° (21), 135-140° (10); note that  $\bar{C}$  is reduced by  $SO_2$  + aq. only in s.t. at 130-140° (10). — Note that  $\bar{C}$  with aq.  $K_2SO_3$  or aq.  $KHSO_3$  soln. replaces both chlorine atoms giving (10) K salt of 4-hydroxy-2,3-disulfonaphthyl-1 sulfuric acid [Beil. XI-304].]

$\bar{C}$  on oxidn. with boilg.  $\text{HNO}_3$  ( $D = 1.35$ ) slowly yields (10) phthalic acid (1:0820).— $\bar{C}$  with aqua regia htd. in s.t. yields (22) phthalic (or nitrophthalic) acid accompanied by some trichloronaphthoquinone-1,4 [Beil. VII-730], yel. ndls., m.p. 250°.

$\bar{C}$  with equal wt  $\text{MnO}_2 + 4.8$  wts conc.  $\text{HCl}$  in s.t. at 230° for 10 hrs. (11) cf. (17) yields 2,2,3,3-tetrachloro-1,4-dioxonaphthalene tetrahydride-1,2,3,4 [Beil. VII-702], colorless pr. from ether, m.p. 117° (11).

$\bar{C}$  with  $\text{PCl}_5$  (2 moles) dislvd. in  $\text{POCl}_3$  htd. in s.t. at 180–200° (10), or at 200–250° for 4–5 hrs (22) (with slow rise of temp. to avoid explosion), yields 1,2,3,4,5-pentachloronaphthalene [Beil. V-546], colorless ndls. from alc., m.p. 168.5° (10) (22).

$\bar{C}$  with large excess  $\text{MeMgI}$  in ether gives (45% yield (23)) (by replacement of 1 atom of chlorine and usual reactn. of the two carbonyl groups) 1,2,4-trimethyl-1,4-dihydroxy-3-chloro-1,4-dihydronaphthalene, cryst. from ether by pptn. with pet. ether, m.p. 115–117° (23); with certain other  $\text{RMgX}$  cpds, however, both chlorine atoms are replaced, e.g.,  $\bar{C}$  with large excess  $\text{C}_6\text{H}_5\text{MgBr}$  in ether gives (34% yield (23)) 1,2,3,4-tetraphenyl-1,4-dihydroxy-1,4-dihydronaphthalene, cryst. from  $\text{C}_6\text{H}_6 + \text{alc.}$ , m.p. 241.5° (23); with still other  $\text{RMgX}$  cpds, neither halogen is affected and only the carbonyl groups react; e.g.,  $\bar{C}$  with large excess  $\alpha\text{-C}_{10}\text{H}_7\text{MgBr}$  in ether gives (75% yield (23)) 1,4-di- $\alpha$ -naphthyl-1,4-dihydroxy-2,3-dichloro-1,4-dihydronaphthalene, m.p. 261° dec. (23).]

$\bar{C}$  with 2 pts.  $\text{Cu}$  powder htd. in nitrobenzene or at 240° as directed (24) gives 3% yield triphthaloylbenzene (1,2,3,4-diphthaloylanthraquinone).— $\bar{C}$  with  $\text{HBr}$  in nitrobenzene htd. in pres. of  $\text{CuCl}_2$  yields (25) 2-bromo-3-chloronaphthoquinone-1,4, m.p. 206–207° (25).

$\bar{C}$  with 2,3-dimethylbutadiene-1,3 (1:8050) in pres. of excess 5% alc.  $\text{KOH}$  and a little sodium hydrosulfite boiled 2 hrs. and then oxidized with air gives (26) 2,3-dimethylanthraquinone [Beil. VII-815, VII-425], yel. ndls. from alc., m.p. 205–206°.]

$\bar{C}$  with boilg. alc.  $\text{KOH}$  hydrolyzes 1 chlorine yielding on acidification (10) 3-chloro-2-hydroxynaphthoquinone-1,4 [Beil. VIII-304], yel. ndls. from alc., m.p. 215°; note that  $\bar{C}$  with  $\text{NaOAc}$  htd. in alc. yields (27) the corresp. acetate, viz., 3-chloro-2-acetoxynaphthoquinone-1,4, yel. ndls. from hot alc., m.p. 98° (27).—[For reactn. of  $\bar{C}$  with  $\text{Na}_2\text{S}$  or with  $\text{H}_2\text{S}$  leading to bimolecular condensation with formn. of dibenzothianthrene diquinone or its deriva. see (28) (8).]

$\bar{C}$  with phenol (2 moles) + dry  $\text{K}_2\text{CO}_3$  (i.e.,  $\text{K}$  phenolate) htd. for 1 hr. at 100° gives (96% yield (2)) 2,3-diphenoxynaphthoquinone-1,4, or-yel. ndls. from xylene, m.p. 205° (2).—[For reactn. of  $\bar{C}$  with pyrocatechol (1:1520) in pres. of diethylamine (2), with pyrogallol (1:1555) in pres. of pyridine (29), or with various anthrols and pyridine in prepn. of vat dyes (30) see indic. refs.]

$\bar{C}$  in nitrobenzene treated with  $\text{NH}_3$  gas or  $\bar{C}$  in boilg. alc. treated dropwise with conc.  $\text{NH}_4\text{OH}$  (27) gives (probably by 1,4-addition and subsequent loss of 1  $\text{HCl}$  (31)) (80% yield (2)) 3-chloro-2-aminonaphthoquinone-1,4, yel.-br. ndls. from  $\text{AcOH}$ , m.p. 193° (2) (corresp. acetyl deriv., m.p. 219° (27)).—Similarly,  $\bar{C}$  with aniline (2 moles) in hot alc. gives (87% yield (12)) (32) 3-chloro-2-anilinonaphthoquinone-1,4 [Beil. XIV-168, XIV-434], copper-red ndls., m.p. 202° (32).—[For corresp. reactn. of  $\bar{C}$  with many other aliphatic or arom. amines see (33), with  $\beta$ -naphthylamine see (34), with  $p$ -phenylenediamine (or its monoacetyl deriv.) see (12); with  $p$ -chloroaniline see (27); note that some amines, e.g.,  $o$ -nitroaniline, 2-aminoanthraquinone, and 3-chloro-2-aminonaphthoquinone do not undergo this reactn. (27).—For reactn. of  $\bar{C}$  with pyridine see (2).]

$\bar{C}$  on nitration, e.g., with 4 vol/pts. red fuming  $\text{HNO}_3$  ( $D = 1.52$ ) +  $2\frac{1}{2}$  vol/pts. pure conc.  $\text{H}_2\text{SO}_4$  at 100° for 6 hrs. (35) cf. (36), gives (40–45% yield (35)) 5-nitro-2,3-dichloronaphthoquinone-1,4, pale yel. cryst. from  $\text{CHCl}_3$  (35),  $\text{AcOH}$  (36), or alc. (36), m.p. 175° (35) (36); this prod. with aniline (2 moles) in hot alc. yields (35) 3-chloro-2-anilino-5 (8)-nitronaphthoquinone-1,4, lfts. from nitrobenzene, m.p. 273° (35).

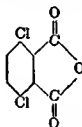
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### 3:4860 3,6-DICHLOROPHTHALIC ANHYDRIDE


 $C_6H_2O_3Cl_2$ 

Beil. XVII - 483  
XVII<sub>1</sub>-(254)

M.P. 193.5-194.5° cor. (1)

191° cor. (2)

190-191° (3)

187° (4)

184-186° (5)

185° (6) (7)

B.P. 339° (3)

[See also 3,6-dichlorophthalic acid (3:4870).]

Long colorless ndls. — Sublimes.

[For prepn. of  $\bar{C}$  from 3,6-dichlorophthalic acid (3:4870) by htg. at 130-140° (2) (3) (4), at 160° (8), at 180-190° (5), by distn. under diminished press. (9), or by htg. in a current of dry air at 40° (7) (10) see indic. refs.: from ethyl hydrogen 3,6-dichlorophthalate by htg. at 200-220° see (2) (5); for foran. of  $\bar{C}$  (together with other isomers) from phthalic anhydride (1:0725) with  $Cl_2$  in pres. of Fe or Fe salts at 160-260° (11) or with  $Cl_2$  in fung  $H_2SO_4$  (12) in pres. of  $I_2$  (3), or from 3-chlorophthalic anhydride (3:3900) with  $Cl_2$  in fung.  $H_2SO_4$  in pres. of  $I_2$  (3), see indic. refs.]

[For sepn. of  $\bar{C}$  from isomeric dichlorophthalic anhydrides by means of salts of corresp. acids, etc., see (3) (13) (1); by means of differential hydrolysis with  $H_2SO_4$  (prods. with no  $\alpha$ -chlorine such as 4,5-dichlorophthalic anhydride require  $H_2SO_4$  of 98-100% concn., those with 1  $\alpha$ -chlorine such as 3,4-dichlorophthalic anhydride hydrolyze with 56-95%  $H_2SO_4$ , those with 2  $\alpha$ -chlorine atoms such as  $\bar{C}$  or 3,4,5,6-tetrachlorophthalic anhydride hydrolyze at  $H_2SO_4$  concns. of less than 50%) see (14).]

$\bar{C}$  dislvd. in abs. EtOH yields the acid ester, viz., ethyl hydrogen 3,6-dichlorophthalate,

cryst. from  $\text{CCl}_4$ , m p  $130\text{--}131^\circ$  (3),  $128\text{--}130^\circ$  (2),  $128\text{--}129^\circ$  (5); note that this ester when dislvd. in EtOH and satd with HCl gas, then warmed, does not convert to the neutral ester readily, and that even with 15 pts. EtOH and 7 hr. htg. only 16% diethyl 3,6-dichlorophthalate is formed (2)

[ $\bar{C}$  with 1 mole  $\text{PCl}_5$  htd in s.t. at  $160^\circ$  for 6-7 hrs. (8) or at  $200^\circ$  for 6 hrs. (15) yields pseudo-3,6-dichlorophthaloyl dichloride (3,3,4,7-tetrachlorophthalide), cryst. from  $\text{C}_6\text{H}_6$ , m p.  $122^\circ$  (15), this prod. upon htg. above its m p., or upon solution in inert solvents, or very rapidly upon treatment of such solns. with decolorizing carbon, or slowly even in solid condition, isomerizes to *sym*-3,6-dichlorophthaloyl dichloride, colorless pr., m.p.  $31^\circ$  (15), from low-boilg. pet. ether (in which the pseudo-chloride is spar. sol.). — With MeOH the pseudo chloride yields the pseudo dimethyl ester (4,7-dichloro-3,3-dimethoxyphthalide, m p  $134^\circ$  (15); the neutral dimethyl 3,6-dichlorophthalate (corresp. to the *sym*-chloride) has m p  $82^\circ$  (15)] — [ $\bar{C}$  with 2 moles  $\text{PCl}_5$  htd in s.t. several hrs. at  $200^\circ$  is claimed (8) to yield a prod.  $\text{C}_8\text{H}_2\text{OCl}_6$ , ndls. from nlc, m p  $117^\circ$  (8)]

[ $\bar{C}$  with 1 mole  $\text{NH}_4\text{OH} \cdot \text{HCl} + \text{Na}_2\text{CO}_3$  in aq. as directed (3) for 3,4-dichlorophthalic anhydride (3:4880) yields 3,6-dichlorophthalylhydroxylamine (*N*-hydroxy-3,6-dichlorophthalimide) [Beil. XXI-504], ndls. from MeOH, m p.  $253\text{--}258^\circ$  (3); the conv. of this prod. with boilg. aq.  $\text{Na}_2\text{CO}_3$  to 3,6-dichloroanthranilic acid (analogous to the corresp. process with its isomers) has not been reported (see, however, under the imide below).]

[ $\bar{C}$  with steam passed over cat. at  $350\text{--}420^\circ$  loses  $\text{CO}_2$  presumably yielding (16) 2,5-dichlorobenzoic acid (3:4340).]

$\bar{C}$  with  $\text{AlCl}_3 + \text{C}_6\text{H}_6$  yields (8) (17) 3,6-dichloro-2-benzoylbenzoic acid [Beil. X-750, X<sub>1</sub>-(357)], ndls. from  $\text{C}_6\text{H}_6$  (17) or dil. alc (8), m.p.  $168.5^\circ$  (18), cor. (17),  $150^\circ$  (8); this prod. on ring closure by htg. with conc.  $\text{H}_2\text{SO}_4$  (2) (17) (18) (19) yields 1,4-dichloroanthraquinone [Beil. VII<sub>1</sub>-(411)], yel. ndls. from AcOH, m p.  $187.5\text{--}188^\circ$  (20),  $187.5^\circ$  cor. (17),  $187.5^\circ$  (18),  $186^\circ$  (19). — [For corresp. reactns. of  $\bar{C} + \text{AlCl}_3$  with chlorobenzene (22), with toluene (21), with *o*-chlorotoluene (3:8215) (23), with *p*-chlorotoluene (3:8287) (24), with fluorene (25), with acenaphthene (26), with pyrene (27), or with  $\beta$ -methylbenzanthrone (28) see indie refs.]

[ $\bar{C}$  with hydroquinone (1:1590) +  $\text{H}_2\text{BO}_3$  htd. at  $190^\circ$  and afterward treated with hot conc.  $\text{H}_2\text{SO}_4$  (29), or htd. with  $\text{AlCl}_3 + \text{NaCl}$  at  $200\text{--}220^\circ$  for 20 min (30), gives (yield: 30% (29), 84% (30)) 5,8-dichloro-1,4-dihydroxyanthraquinone (5,8-dichloroquinizarin) [Beil. VIII<sub>1</sub>-(715)], cryst. from xylene (30) or AcOH (29), m p.  $275.5^\circ$  (30),  $266^\circ$  (29) (diacetate, m p.  $180^\circ$  (30),  $170^\circ$  (29))] — [For reactn. of  $\bar{C}$  with  $\text{AlCl}_3 + o$ -cresol (31), with *o*-cresol methyl ether (31) (19), or with *p*-cresol (7) see indie refs.; for reactn. of  $\bar{C}$  with  $\alpha$ -naphthol +  $\text{H}_2\text{BO}_3$  see (9)]

[ $\bar{C}$  in fumg.  $\text{H}_2\text{SO}_4$  treated with  $\text{Br}_2$  yields (33) (34) 3,6-dichloro-4,5-dibromophthalic anhydride, colorless ndls. from AcOH, m p.  $269\text{--}270^\circ$  (34),  $261^\circ$  (33). —  $\bar{C}$  in fumg.  $\text{H}_2\text{SO}_4$  (50%  $\text{SO}_3$ ) htd. with  $\text{I}_2$  as directed (32) gives (97% yield) 3,6-dichloro-4,5-diiodophthalic anhydride, yel. pr. from AcOH, m p.  $258^\circ\text{--}258.5^\circ$  cor. (32)]

[For condens. of  $\bar{C}$  with substituted *m*-aminophenols in prepn. of phthalein dyestuffs see (35); for use of  $\bar{C}$  in prepn. of pigments of phthalocyanine type see (36) (37); for use of  $\bar{C}$  as plasticizer for cellulose esters see (38).]

Fused  $\bar{C}$  treated with dry  $\text{NH}_3$  gas (39) or with urea (37) yields 3,6-dichlorophthalimide [Beil. XXI-504], ndls. from alc., m p.  $242^\circ$  (19). [This prod. on ring opening and Hofmann degradation with aq. alk.  $\text{NaOCl}$  (3) or  $\text{NaOBr}$  (39) gives 3,6-dichloroanthranilic acid [Beil. XIV-367], ndls. from aq. or AcOH, m p.  $153^\circ$  cf. (3). — [For behavior of  $\bar{C}$  with hydrazine hydrate yielding acc. to conditions *N*-amino-3,6-dichlorophthalimide, *N*-(3,6-dichlorophthalimido)-3,6-dichlorophthalimide, or 3,6-dichlorocyclophthalhydrazide see (40)]

$\bar{C}$  (1 pt.) dislvd. in 5 pts. boilg. AcOH and treated with 1 pt. aniline gives on cooling (82% yield (1)) 3,6-dichlorophthalanil [Beil. XXI<sub>1</sub>-(391)], pale yel. lfts. or ndls. from AcOH, m.p. 201° (10), 197-198° cor. (1), 194° (41), 191° (39). [Note, however, that on protracted htg. with excess aniline first one and then the other nuclear halogen also reacts yielding, respectively, 3-anilino-6-chlorophthalanil, unstable form, m.p. 141° cor. (1), stable form., m.p. 160-160.5° cor. (1), and 3,6-dianilinophthalanil, m.p. 197° (41).]

$\bar{C}$  on saponification with standard alk. (Sap. Eq. = 108.5), followed by acidification, yields 3,6-dichlorophthalic acid (3:4870) q.v.

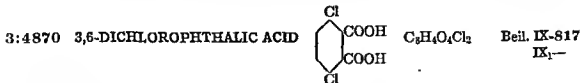
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(31) Mariott, Robinson, *J. Chem. Soc.* 1934, 1633. (32) Pratt, Perkins, *J. Am. Chem. Soc.* 40, 234 (1918). (33) Juvalta, Ger. 50,117, *Friedländer* II-93. (34) Lesser, Weiss, *Ber.* 46, 3945 (1913). (35) Durand, Hueguenin, S.A. Brit. 251,644, July 7, 1926; *Cent.* 1927, I 1228. (36) Imperial Chem. Ind., Ltd., French 808,845, Feb. 16, 1937; *Cent.* 1937, II 3820. (37) Imperial Chem. Ind., Ltd., Thorpe, Linstead, Brit. 390,119, April 27, 1933; French 737,392, Dec. 10, 1932; *Cent.* 1933, II 794. (38) Dreyfus, French 749,792, July 29, 1933; *Cent.* 1934, I 3154. (39) Graebe, Gourevitz, *Ber.* 33, 2024-2025 (1900). (40) Drew, Pearman, *J. Chem. Soc.* 1937, 31-32.

(41) Mariott, Robinson, *J. Chem. Soc.* 1939, 137-138.



M.P. See text.

[See also 3,6-dichlorophthalic anhydride (3:4860).]

Tbls. from aq.; eas. sol. hot aq. in which it readily gives supersatd. solns.; eas. sol. alc., ether.

$\bar{C}$  on htg. begins to lose aq. even at 100° with formn. of 3,6-dichlorophthalic anhydride (3:4860) cf. (1); this change proceeds with increasing speed as the temperature increases; for this reason no definite m.p. of  $\bar{C}$  is recorded and the m.p. observed is actually that of the anhydride.

[For prepn. of  $\bar{C}$  from 3,6-dichlorophthalic anhydride by hydrolysis see the anhydride

(3:4860); from ethyl hydrogen 3,6-dichlorophthalate by htg. at 200° to convert to the anhydride and hydrolysis of the latter see (1); from 1,4-dichloronaphthalene (3:1655) by boilg. with  $\text{HNO}_3$  ( $D = 1.3$ ) see (2); from 1,4,5-trichloronaphthalene (3:4005) by htg. with  $\text{HNO}_3$  in s.t. see (3); from " $\alpha$ -tetrachloronaphthalene" [Beil. V-546] by oxidn. with  $\text{HNO}_3$  see (4); from 1,4-dichloronaphthalene tetrachloride (1,2,3,4,5,8-hexachlorotetraim) [Beil. V-493] by boilg. with conc.  $\text{HNO}_3$  ( $D = 1.42$ ) see (5) (6); from 5,8-dichloronaphthylamine-2 [Beil. XII-1310] on oxidn. with dil.  $\text{HNO}_3$  in s.t. at 180-200° see (7).]

[For sepn. of  $\bar{C}$  from mixts. with the isomeric 3,4- (3:4880) and 4,5- (3:4890) dichlorophthalic acids see (8) (9).] [For use of  $\bar{C}$  as softener and/or plasticizer for cellulose derivs. see (10).]


Salts.  $\text{NH}_4\bar{A}$ ,  $\text{Na}\bar{A}$ ,  $\text{K}\bar{A}$ , as well as  $(\text{NH}_4)_2\bar{A}$ ,  $\text{Na}_2\bar{A}$ , and  $\text{K}_2\bar{A}$ , are all eas. sol. aq. (8);  $\text{Ag}\bar{A}$ , insol. aq. (8) (12);  $\text{Ca}\bar{A}$ ,  $4\text{H}_2\text{O}$  (5) (12), spar. sol. aq. and pptd. by  $\text{CaCl}_2$  from hot dil. aq. solns. of  $(\text{NH}_4)_2\bar{A}$  (8) (12);  $\text{Ba}\bar{A}$ ,  $\text{H}_2\text{O}$ , spar. sol. aq. (5) (12);  $\text{Zn}\bar{A}$ , eas. sol. aq. (characteristic dif. from 3,4- and 4,5-dichlorophthalic acids and used in sepn. of  $\bar{C}$  (8)).

Esters. Dimethyl 3,6-dichlorophthalate, m p 82° (11) (from  $\text{Ag}\bar{A}$  with  $\text{MeI}$  (11)); methyl hydrogen 3,6-dichlorophthalate, unreported; diethyl 3,6-dichlorophthalate, cryst. from 50% alc., m p 60° (12) (13) (from  $\text{Ag}\bar{A}$  on htg. with  $\text{EtI}$  in s.t. at 100° (12) (13), or in very small yield from ethyl hydrogen 3,6-dichlorophthalate with  $\text{EtOH}$  (1) (14)); ethyl hydrogen 3,6-dichlorophthalate, cryst. from  $\text{CCl}_4$ , m p. 130-131° (8), 128-130° (1), 128-129° (15) (from 3,6-dichlorophthalic anhydride (3:4860) with  $\text{EtOH}$ ).

[For studies of ionization consts. of first (16) and second (16) (17) acid groups see indie. refs.]

3:4870 (1) Graebe, *Ber.* 33, 2020-2023 (1900). (2) Atterberg, *Bull. soc. chim.* (2) 27, 409 (1877); *Ber.* 10, 517 (1877). (3) Atterberg, *Bull. soc. chim.* (2) 27, 407 (1877); *Ber.* 9, 1734-1735 (1876). (4) Widman, *Bull. soc. chim.* (2) 28, 511-512 (1877). (5) Faust, *Ann.* 160, 64-65 (1871). (6) Widman, *Ber.* 15, 2160 (1882). (7) Claus, Philipson, *J. prakt. Chem.* (2) 43, 61 (1891). (8) Vilhiger, *Ber.* 42, 3539-3539 (1909). (9) Hodgson, *J. Soc. Dyers Colourists* 49, 215 (1933). (10) Dreyfus, *French* 749,792, July 29, 1933, *Cent.* 1934, 1 3154.

(11) Kirpal, Galuschka, Lasnak, *Ber.* 68, 1332-1334 (1935). (12) Le Royer, *Ann.* 238, 351-354 (1887). (13) Graebe, Gourevits, *Ber.* 33, 2024 (1900). (14) Graebe, Rostorzew, *Ber.* 34, 2108-2109 (1901). (15) Pfeiffer, *Ber.* 55, 425 (1922). (16) Wegscheider, *Monatsh.* 23, 325-326 (1902). (17) Berger, *Helv. Chim. Acta* 23, 41-44, 50-52 (1940).

3:4875 TETRACHLOROPYROCATECHOL   $\text{C}_6\text{H}_2\text{O}_2\text{Cl}_4$  *Beil.* VI - 784  
(Tetrachlorocatechol,  
tetrachloro-1,2-dihydroxybenzene)  $\text{VI}_1$ -(389)  
 $\text{VI}_2$ -(787)

M.P. 101-105° (1)  
104° (2)  
103-101° (3)

[See also tetrachlorobenzoquinone-1,2 (3:3965).]

Colorless anhydrous cryst. from hot dil. alc. (1), lgr. (1) or  $\text{C}_6\text{H}_6$  (2);  $\bar{C}$  from dil.  $\text{AcOH}$  seps. as monohydrate which over  $\text{CaCl}_2$  loses half of its water and above 70-80° all of its aq. (3) (4);  $\bar{C}$  from  $\text{AcOH}$  seps. as a cpd.,  $\bar{C}\cdot\text{AcOH}$ , m.p. 123-124° (3), which can be recrystd. unchanged from lgr. but in air or more rapidly over alk. loses its cryst.  $\text{AcOH}$ ; the above cpd. on soln. in alc. and pptn. with much aq. yields a trihydrate,  $\bar{C}\cdot 3\text{H}_2\text{O}$ , m p. 91°, which can be recrystd. unchanged from aq., alc., or acetone but which from  $\text{C}_6\text{H}_6$  or lgr. seps.  $\bar{C}$  in anhydrous form (4).

[For prepa. of  $\bar{C}$  from pyrocatechol (1:1520) with  $\text{Cl}_2$  in  $\text{AcOH}$  (5) (2) (13) or with  $\text{ICl}$

(3) see indic. refs.; from hexachlorocyclohexene-3-dione-1,2 [Beil. VII-575] by reductn. with  $\text{SnCl}_2$  in  $\text{AcOH}$  see (1).]

$\bar{\text{C}}$  with std. alk. (using phenolphthalein) titrates sharply as a monohydric phenol (4) (6), i.e., Neut. Eq. 248; similarly titration of the cpd.  $\bar{\text{C}}\cdot\text{AcOH}$  (above) gives Neut. Eq. 154 (4).

$\bar{\text{C}}$  on oxidn. with fuming  $\text{HNO}_3$  in  $\text{AcOH}$  gives (81% yield (13)) (1) (5) (7) (8) tetrachloro-*o*-benzoquinone-1,2 (3:3965). — For study of oxidn.-reductn. potential of system:  $\bar{\text{C}}$  + tetrachlorobenzoquinone-1,2 see (7) (8). —  $\bar{\text{C}}$  with equiv. tetrachlorobenzoquinone-1,2 (3:3965) in least possible hot  $\text{CHCl}_3$  gives on cooling the corresp. quinhydrone (14). — [For other complex prods. obt'd. from  $\bar{\text{C}}$  by action of conc.  $\text{HNO}_3$  or  $\text{N}_2\text{O}_4$  (9),  $\text{HNO}_3$  +  $\text{H}_2\text{SO}_4$  (10), or  $\text{NaNO}_2$  in  $\text{AcOH}$  (2) see indic. refs.]


⑤ Tetrachloropyrocatechol diacetate: ndls. from  $\text{AcOH}$ , m.p.  $190^\circ$  (1). [From  $\bar{\text{C}}$  with  $\text{Ac}_2\text{O}$  (1).]

— Tetrachloropyrocatechol monomethyl ether (tetrachloroguaiacol) [Beil. VI-784]: ndls. from hot aq., m.p.  $185\text{--}186^\circ$  (11). [Reported only by indirect means (11).]

— Tetrachloropyrocatechol dimethyl ether (tetrachloroveratrole) [Beil. VI-784]: ndls. from alc., m.p.  $88^\circ$  (11) (12). [Reported only by indirect means (11) (12).]

3:4875 (1) Zincke, Küster, *Ber.* 21, 2729-2730 (1888). (2) Frejka, Sefranek, Zika, *Collection Czechoslov. Chem. Commun.* 9, 241-242 (1937); *Cent.* 1937, II 1816; *C.A.* 31, 7046-7047 (1937). (3) Jackson, Boswell, *Am. Chem. J.* 35, 528-531 (1906). (4) Willstätter, Müller, *Ber.* 44, 2156 (1911). (5) Zincke, *Ber.* 20, 1779 (1887). (6) Weissberger, *Ber.* 65, 1820 (1932). (7) Conant, Fieser, *J. Am. Chem. Soc.* 46, 1873, 1875 (1924). (8) Kvalnes, *J. Am. Chem. Soc.* 56, 2487-2489 (1934). (9) Zincke, *Ann.* 435, 101-162 (1924). (10) Zincke, Weishaupt, *Ann.* 437, 93-94 (1924).

(11) Brüggemann, *J. prakt. Chem.* (2) 53, 251 (1896). (12) Cousin, *Ann. chim.* (7) 29, 57 (1903). (18) Jackson, MacLaurin, *Am. Chem. J.* 37, 11 (1907). (14) Jackson, Carleton, *Am. Chem. J.* 39, 497 (1908).

3:4880 3,4-DICHLOROPHTHALIC ACID   $\text{C}_6\text{H}_2\text{O}_4\text{Cl}_2$  Beil. IX-817  
IX—

M.P. abt.  $195^\circ$  rap. htg. (1)

[See also 3,4-dichlorophthalic anhydride (3:3695).]

Rectangular thls. from aq.; eas sol. aq., ether —  $\bar{\text{C}}$  can only with difficulty be separated from 4,5-dichlorophthalic acid (3:4890) by crystn. (1).

[For prepn. from 3,4-dichlorophthalic anhydride (3:3695) on boilg. with aq. see (1); from *N*-(hydroxy)-3,4-dichlorophthalimide (see under 3,4-dichlorophthalic anhydride) by hydrolysis with hot 10%  $\text{HCl}$  see (1).]

[For sepn. of  $\bar{\text{C}}$  from mixts. with the isomeric 3,6- (3:4870) and 4,5- (3:4890) dichlorophthalic acids see (1) (2).]

Salts.  $\text{NaH}\bar{\text{A}}$ ,  $\text{Ag}\bar{\text{A}}$ ,  $\text{Cu}\bar{\text{A}}$ ,  $\text{Ca}\bar{\text{A}}$ ,  $\text{Ba}\bar{\text{A}}$ ,  $\text{Zn}\bar{\text{A}}$  all spar. sol. aq. (1).

Esters. Methyl hydrogen 3,4-dichlorophthalate and dimethyl 3,4-dichlorophthalate are both unreported; both possible ethyl hydrogen 3,4-dichlorophthalates are known, viz., ethyl 2-carboxy-3,4-dichlorophthalate (from  $\bar{\text{C}}$  + abs.  $\text{EtOH}$  + few drops conc.  $\text{H}_2\text{SO}_4$  refluxed 6 hrs. (3)), ndls. from dil. alc., m.p.  $184^\circ$  (3); and 3,4-dichloro-2-carbethoxybenzoic acid (from diethyl 3,4-dichlorophthalate by partial  $\text{KOH}$  saponification or from the anhydride with abs.  $\text{EtOH}$  (3)), pr. from dil. alc., m.p.  $164^\circ$  (3); diethyl 3,4-dichlorophthalate (from  $\text{Ag}_2\bar{\text{A}}$ ), m.p.  $80^\circ$  (3). [For the *pseudo* diethyl ester of  $\bar{\text{C}}$  see under 3,4-dichlorophthalic anhydride (3:3695).]

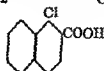
$\bar{C}$  on protracted htg. at 220° loses aq. yielding 3,4-dichlorophthalic anhydride (3:3695) q.v.

3:4880 (1) Villiger, *Ber.* 42, 3538-3539, 3541-3542 (1909). (2) Hodgson, *J. Soc. Dyers Colourists* 49, 215 (1933). (3) Kirpal, Galuschka, Lassak, *Ber.* 68, 1333-1334 (1935).

### 3:4885 1-CHLORONAPHTHOIC ACID-2

 $C_{11}H_7O_2Cl$ 

Beil. IX - 661

IX<sub>1</sub>—

M.P. 196° (1) (2)

195° (3)

Ndls. from  $C_6H_6$  (1) (2) or from 50% AcOH (3). — Volatile without decompn. (1).

[For prepn. of  $\bar{C}$  from 2-(1-chloronaphthyl)carbinol (2) by oxidn. see (2); from 1-chloro-2-(trichloromethyl)naphthalene [Beil. V-568] by hydrolysis in boilg. AcOH contg. a little aq. see (1), from 1-chloro-2-naphthonitrile (see below) by hydrolysis with AcOH/ $H_2SO_4$ /aq. mxt. see (4), from methyl 1-chloro-2-naphthoate (see below) by hydrolysis with boilg. 15% alc. KOH (46% yield) see (3)]

$\bar{C}$  with 2% Na/Hg in aq. reduces (1) to  $\beta$ -naphthoic acid (1:0800), m.p. 184° (1).

[The direct conv. of  $\bar{C}$  to 1-chloro-2-naphthoyl chloride is not actually reported; however, this acid chloride, m.p. 59-60.5° (5), b.p. 226° at 150 mm. (5), b.p. 199-200° at 11.2 mm (5), has been obtained (5) (3) (6) from 1-hydroxy-2-naphthoic acid [Beil. X-331, XI-(145)] with  $PCl_5$  (yield 60.7% (5)) (2)]

Salts.  $Ag\bar{A}$ , white floccs spar sol. aq.,  $Ca\bar{A}_2 \cdot 2H_2O$ , cryst. from aq. (1).

— Methyl 1-chloro-2-naphthoate: ndls. from alc., m.p. 50° (2), cryst. from pet. eth. + acetone, m.p. 44-48° (5), b.p. 189-193° at 17.5 mm (3), 186.5-189° (but press. not given) (5). [From  $\bar{C}$  in MeOH with  $HCl$  gas (2) or from the acid chloride (above) in boilg. MeOH (5) (3).] [This ester with Cu bronze + a trace of  $I_2$  at 200° yields (5) dimethyl 1,1'-binaphthyl-2,2-dicarboxylate]

— Ethyl 1-chloro-2-naphthoate: unreported.

— 1-Chloro-2-naphthonitrile: colorless ndls. from MeOH but m.p. not stated (4), b.p. 183-184° at 11 mm (4). [From 1-chloro-2-naphthylamine [Beil. XII-1308, XII<sub>1</sub>-(542)] by diazotization and reactn. with  $KCu(CN)_2$  (4).]

3:4885 (1) Wolfenstein, *Ber.* 21, 1190-1191 (1888). (2) Achmatowicz, Lindenfeld, Roczniki Chem. 18, 69-74 (1934); *Cent.* 1939, II 389, not in C.A. (3) Bergmann, Hershberg, *J. Chem. Soc.* 1936, 333. (4) Willstaedt, Scheiber, *Ber.* 67, 473-474 (1934). (5) Kuhn, Albrecht, *Ann.* 463, 283-285 (1928). (6) Strohbach, *Ber.* 34, 4181 (1901).

### 3:4890 4,5-DICHLOROPHTHALIC ACID

 $C_6H_2O_4Cl_2$ 

Beil. IX - 818

IX<sub>1</sub>-(366)

M.P. 199-200° (1)

200° rap. htg. (2)

[See also 4,5-dichlorophthalic anhydride (3:4830).]

Ndls. from aq.

[For prepn. of  $\bar{C}$  from 4,5-dichlorophthalic anhydride (3:4830) by hydrolysis see (2)]



(3); from aq. soln. of alk. salts of phthalic acid (1:0820) with  $\text{Cl}_2$  in pres. of Sb cpds. see (3) (4); from 4,5-dichloro-1,2-dimethylbenzene (1) by oxidn. with dil.  $\text{HNO}_3$  ( $D = 1.3$ ) in s.t. at  $180^\circ$  for 7 hrs. see (1) cf. (5) (6).]

[For sepn. of  $\bar{\text{C}}$  from mixts. with thn isomeric 3,4- (3:4880) and 3,6- (3:4870) dichlorophthalic acids see (2) (8).] — [For use of  $\bar{\text{C}}$  as softener for cellulose derivs. see (9).]

Salts.  $\text{NH}_4\bar{\text{H}}\bar{\text{A}}$ ,  $\text{NaH}\bar{\text{A}}$ ,  $\text{KH}\bar{\text{A}}$  (all from aq. solns. of the corresp. eas. sol. neutral salts by addn. of  $\text{AcOH}$ ) are spar. sol. cold aq. (2):  $\text{Cu}\bar{\text{A}}$ ,  $\text{Ca}\bar{\text{A}}$ ,  $\text{Ba}\bar{\text{A}}$ ,  $\text{Zn}\bar{\text{A}}$ , and  $\text{Ag}_2\bar{\text{A}}$  are all spar. sol. (2).

Esters. Dimethyl 4,5-dichlorophthalate and diethyl 4,5-dichlorophthalate are unreported; methyl hydrogen 4,5-dichlorophthalate is unreported, but ethyl hydrogen 4,5-dichlorophthalate, ndls. from  $\text{CHCl}_3$ , m.p.  $133\text{--}134^\circ$ , is obtained from the anhydride (3:4830) with  $\text{EtOH}$  (2).

[ $\bar{\text{C}}$  on fusion with  $\text{NaOH}$  at  $175\text{--}185^\circ$  gives (small yield (3)) 4,5-dihydroxyphthalic acid [Beil. X-552,  $\text{X}_1$ -(276)], m.p.  $175^\circ$ .

$\bar{\text{C}}$  on htg. loses  $\text{H}_2\text{O}$  yielding (2) 4,5-dichlorophthalic anhydride (3:4830), m.p.  $187^\circ$ .

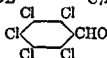
⑩ Di-(*p*-nitrobenzyl) 4,5-dichlorophthalate: cryst. from alc., m.p.  $164.5^\circ$  (10). [From  $\text{Na}_2\bar{\text{A}}$  with *p*-nitrobenzyl bromide (2 moles) btd. in alc. (10).]

3:4890 (1) Hinkel, Ayling, Bevan, *J. Chem. Soc.* 1928, 1876. (2) Villiger, *Ber.* 42, 3538-3539, 3540-3547 (1909). (3) Rushchinskii, *J. Applied Chem. (U.S.S.R.)* 7, 1113-1115 (1934); *Cent.* 1936, II 2902. (4) Rushchinskii, *Russ.* 41,515, *Feh.* 28, 1935; *Cent.* 1935, II 3704; *C.A.* 30, II 2902. (5) Claus, Kautz, *Ber.* 18, 1369-1370 (1885). (6) Claus, Groneweg, *J. prakt. Chem.* (2) 43, 253-254 (1891) (7) *Ref.* 2, pp. 3532-3533. (8) Hodgson, *J. Soc. Dyers Colourists* 49, 215 (1933). (9) Dreyfus, *French* 749,792, July 29, 1933; *Cent.* 1934, I 3154. (10) Lyons, Reid, *J. Am. Chem. Soc.* 39, 1741, 1744 (1917).

### 3:4892 PENTACHLOROBENZALDEHYDE

 $\text{C}_7\text{HOC}_l_5$ 

Beil. VII —

VII<sub>1</sub>-(134)M.P.  $202.5^\circ$  (1) (2) $197\text{--}199^\circ$  (3)

Colorless ndls. from  $\text{C}_6\text{H}_6$ /alc.; eas. sol. hot  $\text{C}_6\text{H}_6$  or  $\text{CS}_2$ ; spar. sol. alc., ether, lgr.

[For prepn. of  $\bar{\text{C}}$  from pentachlorobenzal (di)chloride (3:3590) by hydrolysis with conc.  $\text{H}_2\text{SO}_4$  at  $60\text{--}100^\circ$  or fuming  $\text{H}_2\text{SO}_4$  at  $40\text{--}50^\circ$  (90% yield (2)) (3) see indic. refs.; from pentachlorobenzaldehyde diethylacetal (see below) by acid hydrolysis see (1).]

$\bar{\text{C}}$  with aq. alk.  $\text{KMnO}_4$  refluxed 7 hrs. oxidizes to (90% yield (1)) pentachlorobenzoic acid (3:4910).

$\bar{\text{C}}$  in  $\text{C}_6\text{H}_6$  shaken with satd. aq.  $\text{NaHSO}_3$  soln. gives (1) the corresp.  $\text{NaHSO}_3$  epd.

$\bar{\text{C}}$  with aq. 50%  $\text{KOH}$  at  $100^\circ$  for 5 hrs. suffers hydrolytic cleavage giving (88% yield (2)) pentachlorobenzene (3:2290) and potassium formate.

$\bar{\text{C}}$  with  $\text{EtOH}$  + dry  $\text{HCl}$  gas gives (60% yield (1)) pentachlorobenzaldehyde diethylacetal, colorless cryst. from pet. ether, m.p.  $45^\circ$ .

[For use of  $\bar{\text{C}}$  on prepn. of dyes of the triphenylmethane series see (4).]

$\bar{\text{C}}$  reacts normally with  $\text{RMgX}$  reagents [e.g.,  $\bar{\text{C}}$  with  $\text{McMgBr}$  gives (49% yield (1)) methyl-pentachlorophenyl-carbinol, colorless cryst. from alc., m.p.  $126^\circ$  (1);  $\bar{\text{C}}$  with  $\text{C}_6\text{H}_5\text{MgBr}$  gives (1) phenyl-pentachlorophenyl-carbinol (pentachlorobenzohydrol), cryst. from  $\text{C}_6\text{H}_6$ , m.p.  $117^\circ$ .]

$\bar{\text{C}}$  with anhydrous  $\text{NaOAc}$  +  $\text{Ac}_2\text{O}$  (Perkin synthesis) at  $170\text{--}180^\circ$  for 60 hrs. gives (30% yield (1)) 2,3,4,5,6-pentachlorocinnamic acid, cryst. from  $\text{C}_6\text{H}_6$ , m.p.  $233^\circ$  cor. (1).

$\bar{C}$  with aniline at 100° condenses giving (1) pentachlorobenzaldehyde aml, greenish ndls. from  $C_6H_6$ /alc., m.p. 187.5° cor. (1).

⑥ Pentachlorobenzaldehyde: colorless ndls. from  $C_6H_6$ , m.p. 201° cor. (1). (From  $\bar{C}$  with  $NH_2OH \cdot HCl + Na_2CO_3$  in dil alc. at stdg. few days (1).)

⑦ Pentachlorobenzaldehyde phenylhydrazones: citron-yel. ndls. from alc., m.p. 152.5° cor. (1) [From  $\bar{C}$  in hot satd  $C_6H_6$  soln with 1 mole phenylhydrazine (1).]

—— Pentachlorobenzaldehyde *p*-nitrophenylhydrazones: unreported.

—— Pentachlorobenzaldehyde 2,4-dinitrophenylhydrazones: unreported.

—— Pentachlorobenzaldehyde semicarbazones: unreported.

3:4892 (1) Lock, *Ber* 72, 300-304 (1939). (2) Lock, *Ber* 66, 1533 (1933). (3) Bayer and Co., *Ger* 243,416, Feb. 10, 1912, *Cent* 1912, I 618; [*C.A.* 6, 2292 (1912)] U.S. 998,140, July 18, 1911; [*C.A.* 5, 2904-2905 (1911)] (4) Bayer and Co., *Ger.* 234,519, May 12, 1911; *Cent.* 1911 I 1620; [*C.A.* 5, 2974 (1911)]

3:4893 OCTACHLORONAPHTHALENE  
(Perchloronaphthalene)



$C_{10}Cl_8$

Beil. V - 547

$V_1$ —

$V_2$ -(446)

M.P.		B.P.	
203° (1) u.c.	(8)	440-442° at 764 mm., dec.	(2)
202° u.c.	(7)	258-260° at 2.5 mm.	(2)
209°	(6)	246-250° at 9.6 mm.	(2)
197.5-198° cor.	(2)		
197.3-198° cor.	(3)		

Ndls. from  $CCl_4 + C_6H_6$  (2); fairly eas. sol.  $C_6H_6$ , lgr.,  $CHCl_3$ ; spar. sol. alc. or  $AcOH$ .

[For prepn. of  $\bar{C}$  from naphthalene (1:7200) with  $Cl_2$  in pres. of 1% Fe powder + 9.1%  $I_2$  first at 100° then at 150° for 10-12 hrs (90% yield (2)) or with  $Cl_2$  in pres. of  $SbCl_5$  (1) (4) cf. (2) see indic. refs. (for extensive study of merits of many catalysts see (5)).]

[For prepn. of  $\bar{C}$  from mixt. of 2-hydroxynaphthalene-1,5-bis-(sulfonyl chloride) and 2-hydroxynaphthalene-1,6-bis-(sulfonyl chloride) (from  $\beta$ -naphthol with  $ClSO_3H$ ) with  $PCl_5$  in s.t. see (6), from 1-hydroxynaphthalene-tris-(sulfonyl chloride) with  $PCl_5$  in s.t. at 250° see (7); from 1-amino-3,6,8-tris-(sulfonyl chloride) with 3-4 pts.  $PCl_5$  in s.t. at 200-225° for 7 hrs. (40% yield) see (2).]

[For prepn. of  $\bar{C}$  from 2,5,6,7,8-pentachloronaphthoquinone-1,4 (Beil. VII-731) with  $PCl_5$  in s.t. at 250° for 6 hrs. see (5); from hexachloronaphthoquinone-1,4 (see below) with  $PCl_5$  see (3) ]

[For study of action of  $\bar{C}$  (from insulation material on electric wiring) in production of acne see (9); for prepn. of aq. dispersions of  $\bar{C}$  see (10); for use of  $\bar{C}$  as insecticide see (11); for use of  $\bar{C}$  in prepn. of a red mordant dyestuff (by actn. of fmg.  $H_2SO_4$ ) see (12).]

[ $\bar{C}$  with  $H_2$  passed through a red-hot tube (4) or  $\bar{C}$  with Na +  $EtOH$  (2) gives naphthalene (1:7200) together with other prods.]

$\bar{C}$  on oxidn. with 10 pts. fmg.  $HNO_3$  ( $D = 1.52$ ) in s.t. at 90° gives in good yield (2) (3) hexachloronaphthoquinone-1,4, m.p. 222.5° cor., b.p. 412-415° at 758 mm. dec., 265-267° at 14 mm., accompanied by some tetrachlorophthalic acid (3:4946).

[ $\bar{C}$  on htg. with  $SbCl_5 + ICl$  in s.t. at 350° (1) breaks down yielding (2) cf. (1) carbon tetrachloride (3:5100), hexachloroethane (3:4535), hexachlorobenzene (3:4939), and other prods.; under certain conditions (not specified in abstracts)  $\bar{C}$  can be broken down to decachloroindane (perchlorohydrindene) (Beil. V-487, m.p. 138° cor. (2) ]

[ $\tilde{C}$  with pyridine + CuO + hydrazine hydrate yields (13) a hexachloronaphthalene ndls. from chlorobenzene, m.p. 202-204° (13) (note that m.p. is close to that of  $\tilde{C}$ ).]

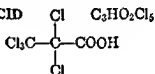
$\tilde{C}$  is stable toward 3% aq. KOH or NaOH for 12 hrs. in cold or even 2 hrs. boilg.;  $\tilde{C}$  is stable to cold 3% alc. KOH or NaOH for 24 hrs., but on htg. for 2 hrs. splits off some 25-30% chlorine and in part resinifies (2).

② Color test with  $SbCl_5$  in  $CCl_4$ :  $\tilde{C}$  with  $SbCl_5$  in  $CCl_4$  gives stable cherry-red color (2).

[This response is not given by carbon tetrachloride (3:5100), hexachloroethane (3:4835), hexachlorobenzene (3:4939), or decachloroindane (2).]

3:4893 (1) Ruoff, *Ber.* 9, 1486-1488 (1876). (2) Shvemberg, Gordon, *J. Gen. Chem. (U.S.S.R.)* 2, 921-928 (1932); *Cent.* 1934, I 215; *C.A.* 27, 2139 (1933). (3) Shvemberg, Gordon, *J. Gen. Chem. (U.S.S.R.)* 4, 695-703 (1934); *Cent.* 1935, II 514; *C.A.* 29, 2162 (1935). (4) Berthelot, Jungfleisch, *Bull. soc. chim.* (2) 9, 446-455 (1868); *Ann. chim.* (4) 15, 330-343 (1868). (5) Shvemberg, Gordon, *J. Gen. Chem. (U.S.S.R.)* 4, 529-551 (1934); *Cent.* 1935, II 514; *C.A.* 29, 1804 (1935). (6) Pollak, Gebauer-Fulnegg, Blumenstock-Halward, *Monatsh.* 49, 199 (1928). (7) Glaus, Mieleke, *Ber.* 19, 1186-1187 (1886). (8) Claus, Wenzlik, *Ber.* 19, 1169 (1886). (9) Haldin-Davis, *Brit. J. Dermatol. Syphilis* 51, 380-383 (1939), *C.A.* 34, 1413 (1940). (10) Heekert (to du Pont Rayon Co.), U.S. 2,060,210, Nov. 10, 1936; *Cent.* 1937, I 1604; *C.A.* 31, 555 (1937). (11) Stern, *Ger.* 411,314, March 26, 1925; *Cent.* 1925, II 234. (12) B.A.S.F., *Ger.* 60,611, *Friedländer* 3, 271. (13) I.G., French 699,492, Feb. 16, 1931; *Cent.* 1931, 3519.

### 3:4895 PENTACHLOROPROPIONIC ACID



Beil. II —

II<sub>1</sub>-(112)

II<sub>2</sub>-(228)

M.P. 200-215° (see text (1)).

Colorless cryst. from  $CCl_4$ . — Eas sol cold aq.

[For prepn. of  $\tilde{C}$  from trichloroacrylic acid (3:1840) with  $Cl_2$  in  $CCl_4$  soln. in sunlight (yield not reported) see (1)]

$\tilde{C}$  in aq. soln. behaves as a strong acid; on titration it gives a good Neut. Eq., calcd. 246.5; found 245.8 (1).

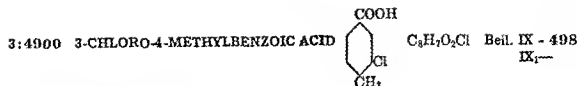
$\tilde{C}$  is very unstable: e.g.,  $\tilde{C}$  in aq. soln. on warming dec. (1) (with loss of HCl and  $CO_2$ ) into tetrachloroethylene (3:5460); presumably this same decompn. occurs on process of taking its m.p., and the value given above refers to rapid htg. on Hg bath.

Salts. The salts of  $\tilde{C}$  can be obtd. by neutralization with metal hydroxide of a cold satd. aq. soln. of  $\tilde{C}$  followed by evapn. to dryness at low temp.; aq. solns. of the salts are also unstable and rapidly decompose yielding metal chloride +  $CO_2$  + tetrachloroethylene (3:5460) (1). [For studies of influence of light on decompn. of these salts see (2) (3) cf. (4).]

[For study of behavior of  $\tilde{C}$  with  $H_2$  + colloidal Pd see (5).]

Acid chloride. Pentachloropropionyl chloride (3:0470) has been obtd. indirectly, i.e., from trichloroacryloyl chloride with  $Cl_2$  in sunlight (6); colorless cryst., m.p. 42°.

3:4895 (1) Boeseken, *Rec. trav. chim.* 46, 841-843 (1927). (2) Jaeger, *J. Chem. Soc.* 119, 2070-2076 (1921). (3) Jaeger, Berger, *Rec. trav. chim.* 41, 72 (1921). (4) Jaeger, *Cent.* 1912, I 1817-1818; *Cent.* 1911, II 1851. (5) Boeseken, *Rec. trav. chim.* 35, 273-274 (1915). (6) Boeseken, Hasselbach, *Rec. trav. chim.* 32, 11-14 (1913).



M.P. 200-202°	(1)
199-201° cor.	(2)
199°	(3)
196°	(4) (5)
195-197°	(6)
194-196° u.c.	(2)
194-195°	(7)

Long colorless ndls. from dil. alc.; spar. sol. hot aq; eas. sol. cold alc.

[For prepn. of  $\bar{C}$  from 2-chloro-4-isopropyl-methylbenzene (2-chloro-p-cymene) (3:8775) by oxidn. with dil.  $HNO_3$  (7) of  $D = 1.24$  for 8-14 days (2) or htd. 6 hrs. with 5 pts.  $HNO_3$  ( $D = 1.39$ ) + 5 pts. aq. (4) see indic. refs; from 3-chloro-1,4-dimethylbenzene (2-chloro-p-xylene) (3:8600) by oxidn. with nitrosulfonic acid + fuming  $HNO_3$  see (1) (5); from 3-chloro-4-methylacetophenone (8) by oxidn. with alk.  $KMnO_4$  see (8); from 3-chloro-4-methylbenzaldehyde (5) with 50%  $KOH$  (Cannizzaro reactn.) see (5); from 3-chloro-4-methylbenzonitrile, m.p. 43-48.5° u.c. (3), 45-46° (6), by protracted boillg. with aq.  $KOH$  see (3), from 3-chloro-4-methylbenzamide (see below) on hydrolysis with 25% aq.  $NaOH$  see (6).]

Salts.  $K\bar{A}.1\frac{1}{2}H_2O$ , eas. sol. aq. (9);  $Ca\bar{A}_2.3H_2O$ ,  $Ba\bar{A}_2.4H_2O$  (7).

$\bar{C}$  on fusion with  $KOH$  yields (7) (2) 3-hydroxy-4-methylbenzoic acid [Beil. X-237].

[ $\bar{C}$  on mononitration (9) yields a mixt. of three mononitro derivs. containing 60-70% 3-chloro-4-methyl-6-nitrobenzoic acid [Beil. IX-503], ndls. from alc., m.p. 184-185° (9), 20-30% 3-chloro-4-methyl-5-nitrobenzoic acid [Beil. IX-503], ndls. from aq., m.p. 159° u.c. (9), and 5-10% 3-chloro-4-methyl-2-nitrobenzoic acid [Beil. IX-503], lfts. from aq., m.p. 211° (9).]

— Ethyl 3-chloro-4-methylbenzoate: oil, b.p. 129-130° at 9 mm.,  $D_4^{20} = 1.1653$ ,  $n_D^{20} = 1.52531$  (10). [Note that for the b.p. 149-150° formerly reported (3) no pressure is given.]

— 3-Chloro-4-methylbenzamide: lfts. from aq., alc., or aq. alc., m.p. 173-175° (6). [From partial hydrolysis of 3-chloro-4-methylbenzonitrile (above) with aq. alk. (3) (6), further hydrolysis yields (6)  $\bar{C}$ .]

3:4900 (1) Varma, Ramon, *J. Indian Chem. Soc.* 12, 541 (1935). (2) Vongerichten, *Ber.* 11, 365-368 (1878). (3) Claus, Davidsen, *J. prakt. Chem.* (3) 39, 497-498 (1889). (4) Hintikka, *Ann. Acad. Sci. Fennicae 2A*, No. 10, 6 pp. (1923), *C.A.* 19, 42 (1925). (5) Wahl, *Compt. rend.* 198, 1613-1614 (1934). (6) Magidson, Trawin, *Ber.* 69, 538-539 (1936). (7) Vongerichten, *Ber.* 10, 1249-1250 (1877). (8) Ganguly, LeFevre, *J. Chem. Soc.* 1934, 852. (9) Claus, Böcher, *Ann.* 265, 356-363 (1891). (10) von Auwers, Hantz, *Z. physik. Chem.* A-143, 17-18 (1929).

**3:4908 4-CHLORO-2-HYDROXYBENZOIC ACID**  $C_7H_5O_3Cl$   
 (4-Chlorosalicylic acid)

 Beil. X - 101  
 XI- (47)

 M.P. [211° (1)]  
       207.5° (2)  
       207° (3) (4)  
       206-207° (5)

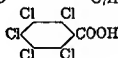
Colorless ndls. from aq.; spar. sol. aq., eas. sol. alc.,  $C_6H_6$ ,  $CHCl_3$ . — Volatile with steam; sublimes with slight decompn.

[For prepn. of  $\bar{C}$  from *m*-chlorophenol (3:0255) by treatment of dry sodium salt with  $CO_2$  at 140-150° under press. see (3); from 4-chloro-2-aminobenzoic acid (4-chloroanthranilic acid) [Beil. XIV-365, XIV<sub>1</sub>-(548)] via diazotization and boilg. with aq. see (3) (5); from 7-chloro-2,3-dimethylchromone [Beil. XVII<sub>1</sub>-(177)] on boilg. with 4% aq. NaOH see (2); for formn. of  $\bar{C}$  from *p*-chlorobenzoic acid (3:4940) by electrolytic oxidn. in acid soln. see (4); from 4-chloro-2-methoxybenzoic acid (see below) by cleavage with HI see (1).]

$\bar{C}$  in aq. soln. gives with  $FeCl_3$  a purple color.

[The methyl ether of  $\bar{C}$ , viz., 4-chloro-2-methoxybenzoic acid, cryst. from aq., m.p. 148° (1), has been obtd. from 4-chloro-2-methoxybenzaldehyde (1) by oxidn. with aq. alk.  $KMnO_4$  (1).]

3:4908 (1) Hodgson, Jenkinson, *J. Chem. Soc.* 1927, 1741-1742. (2) Simonis, Schenkmann, *Ber.* 50, 1146-1147 (1917). (3) Varnholt, *J. prakt. Chem.* (2) 36, 27-31 (1887). (4) Fichter, Adler, *Helv. Chim. Acta* 9, 283 (1920). (5) Cohn, *Mitt. Technol. Gewerb.-Mus. Wien*, 11, 178-182; *Cent.* 1901, I 925.

**3:4910 PENTACHLOROBENZOIC ACID**
 $C_7HO_2Cl_5$ 
 Beil. IX - 347  
 IX<sub>1</sub>-(142)

 M.P. 298° cor. (1)  
       201° (2)  
       200° (3)  
       199-200° u.c. (4)  
       199.5° (5)

Ndls. or pr.; sublimes in vac. with slight decomposition (6). Very sol. toluene or alc. (5). — Best recrystd. from toluene + lt. pet. ether (5). — Can be recrystd. from  $C_6H_6$  or dil. AcOH (6). — From alc.  $\bar{C}$  (despite its high m.p.) first separates as an oil (5).

[For prepn. of  $\bar{C}$  from pentachlorotoluene (3:4937) with conc.  $HNO_3$  + Hg see (5); from pentachlorobenzaldehyde (3:4892) with  $KMnO_4$  (90% yield) see (1); from *asym*-tetrachlorophthalyl chloride +  $Cl_2$  via conversion to and subsequent hydrolysis of pentachlorobenzoyl chloride (3:2295) see (3); from 2,3- (3:4650) or 3,4-dichlorobenzoic acid (3:4925) +  $MnO_2$  + fuming HCl at 180-200° see (4).]

Pentachlorobenzoyl chloride (3:2295), colorless lfts. from alc., m.p. 87° (3), has been prepd. indirectly (see above), but the reaction (if any) of either  $PCl_5$  or  $SOCl_2$  on  $\bar{C}$  has never been reported. Upon hydrolysis with alc. KOH the acid chloride yields  $\bar{C}$  (3).

- Methyl pentachlorobenzoate: pr. from MeOH, m.p. 97° (3). [Prepared from pentachlorobenzoyl chloride + MeOH by 30 hrs. reflux. (3).]  
 — Ethyl pentachlorobenzoate: unrecorded..  
 — Pentachlorobenzamide: unrecorded..  
 — Pentachlorobenzanilide: unrecorded.

3:4910 (1) Lock, *Ber.* 72, 303 (1939). (2) Steiner, *Monatsh.* 36, 827 (1915). (3) Kirpal, Kunze, *Ber.* 62, 2105 (1929). (4) Claus, Bücher, *Ber.* 20, 1627 (1887). (5) Silberrad, *J. Chem. Soc.* 127, 2681 (1925). (6) Eckert, Steiner, *Monatsh.* 36, 187 (1915).

3:4915 4-CHLORO-3-METHYLBENZOIC ACID  $C_8H_7O_2Cl$  Beil. IX-478  
 IX<sub>1</sub>—



M.P. 209-210° cor. (1)	
209-210° (2)	
209.5° cor. (3)	
209° u.c. (4)	
208° (5)	
207-208° (6)	
203° (7) (8)	

Colorless nlls. from hot aq., alm. insol. cold aq.; very spar. sol. even in hot aq.

[For prepn. of  $\bar{C}$  from 4-chloro-1,3-dimethylbenzene (3:8665) by oxidn. with  $K_2Cr_2O_7$  + dil.  $H_2SO_4$  see (5) (1), from 4-chloro-1-ethyl-3-methylbenzene (6) by oxidn. with dil.  $HNO_3$  (1:10) at 100° for 10 hrs. see (6); from 4-chloro-3-methylacetophenone [Beil. VII-307] by oxidn. with alk.  $KMnO_4$  see (4); from 4-chloro-3-methyl- $\omega, \omega, \omega$ -trichloroacetophenone (3) see (3), from  $\beta$ -chloroethyl 4-chloro-3-methylphenyl ketone (5) by oxidn. with mixt. of equal pts. conc.  $HNO_3$  and aq. at 100° see (5); from 1,2-bis-(4-chloro-3-methylbenzoyl)-1,2-dibromoethane (2) by fusion with NaOH see (2); from 4-amino-3-methylbenzoic acid [Beil. XIV-180] via diazotization and use of  $Cu_2Cl_2$  reactn. see (7).]

$\bar{C}$  on fusion with KOH yields (1) 4-hydroxy-3-methylbenzoic acid [Beil. X-225, X<sub>1</sub>-(97)], m.p. 173° (1), together with some 4-hydroxyisophthalic acid [Beil. X-502, X<sub>1</sub>-(256)].

Salts.  $Ca\bar{A}_2 \cdot 3H_2O$  (4),  $Ba\bar{A}_2 \cdot 3H_2O$  (5); both cas. sol. aq.

$\bar{C}$  on further oxidn. with  $KMnO_4$  yields (1) 4-chlorobenzenedicarboxylic acid-1,3 (4-chloroisophthalic acid) (3:4909).

— Ethyl 4-chloro-3-methylbenzoate: oil, b.p. 260-265° (5). [From  $\bar{C}$  in alc. with  $HCl$  gas (5)]

3:4915 (1) Jacobsen, *Ber.* 18, 1761-1762 (1885). (2) Conant, *Ann.* 11, 111 (1925). (3) Houben, Fischer, *Ber.* 64, 2612 (1931). (4) C. (1925). (5) Mayer, Müller, *Ber.* 60, 2251 (1927). (6) " (1921). (7) Beilstein, Kressler, *Ann.* 144, 182 (1907). (8) " (1921).

3:4916 9,10-DICHLOROANTHRACENE  
(*meso*-Dichloroanthracene)

 $C_{14}H_8Cl_2$ 

Beil. V - 664  
V<sub>1</sub>-(324)  
V<sub>2</sub>-(575)

M.P. 210° (1)  
209-210° (2) (3)  
209° (4) (5) (6) (7)  
(8) (9) (10) (23)  
208-209° (11) (12)

*Yellow* ndls. from  $CCl_4$  or  $C_6H_6$  or by sublimation; spar. sol. alc. or ether, eas. sol.  $C_6H_6$ .

[For prepn. of  $\bar{C}$  from anthracene (1:7285) with  $Cl_2$  in *o*-dichlorobenzene (5) (30) polychlorobenzenes of h.p. 140-170° (4), nitrobenzene (4) (5), or in acetylene tetrachloride (5) (yields: 93-94% (4), 87-88% (5)) see indic. refs. (note that numerous attempts to use this reactn. are given in earlier literature (3) (13) (14) (15) (16) (17) (18) (19) (20) but none is well adapted for pure  $\bar{C}$  owing to simultaneous formn. of more highly chlorinated cpds.); from anthracene with  $SO_2Cl_2$  in  $CCl_4$  (7) (11) or in xylene (11) at ord. temp. (yields nlm. quant. (7) (11)) see indic. refs. (note, however, that the results are sometimes influenced by the source of anthracene used (11)); for formn. of  $\bar{C}$  from anthracene (1:7285) with  $Cl_2$ -aq. (21), with  $S_2Cl_2$  (10), or with  $NOCl$  in s.t. at 150° or at room temp. in sunlight (22) see indic. refs.; for formn. of  $\bar{C}$  from anthracene present in crude phenanthrene during treatment of latter in  $CS_2$  with  $Cl_2$  see (12).]

[For prepn. of  $\bar{C}$  from anthrone (9-hydroxyanthracene) [Beil. VII-473, VII<sub>1</sub>-(256)] with 2 wt. pts.  $PCl_5$  in  $C_6H_6$  or without solv. at 100° for 16 hrs. see (2); for formn. of  $\bar{C}$  from 9,9,10,10-tetrachloro-9,10-dihydroanthracene (9,10-dichloroanthracene dichloride-9,10) [Beil. V-641, V<sub>1</sub>-(309)] by actn. of Zn dust, Cu powder, or phenylhydrazine (3) or on hollg. with anthrone (above) in xylene (6) see indic. refs.; for formn. of  $\bar{C}$  from 1,2,3,4-tetrachloro-9,10-dichloroanthracene by htg. with hydrazine hydrate + Cu powder in pyridine (23), or from 9-benzylanthracene with  $SOCl_2$  in  $CHCl_3$  (24), see indic. refs.; from  $\alpha$ -[9,10-dichloroanthracene tetrahydromide-1,2,3,4] (see below) by treatment with Zn dust in AcOH or with Cu powder in  $C_6H_6$  see (3).]

[ $\bar{C}$  with  $Cl_2$  in cold  $CHCl_3$  or acetylene tetrachloride gives (17) 9,9,10,10-tetrachloro-9,10-dihydroanthracene (see above);  $\bar{C}$  with  $Cl_2$  in  $C_6H_6$  at 60° yields (17) 2,3,9,10-tetrachloro-2,3-dihydroanthracene;  $\bar{C}$  in warm  $CHCl_3$  or cold  $C_6H_6$  gives (17) a mixt. of these prods.; the end prod. of chlorination of  $\bar{C}$  in  $C_6H_6$  at 20° appears (16) (3) to be 1,2,3,4,9,10-hexachloro-1,2,3,4-tetrahydroanthracene [Beil. V-611, V<sub>1</sub>-(287)], m.p. 205-207° (3). —  $\bar{C}$  with  $SO_2Cl_2$  in nitrobenzene at 100° yields (25) 2,9,10-trichloroanthracene.]

$\bar{C}$  adds 2 moles  $Br_2$  giving according to conditions one or the other of two isomeric addn. compds.; i.e.,  $\bar{C}$  moistened with  $CHCl_3$  and treated with 2  $Br_2$  yields (3) (8)  $\alpha$ -[9,10-dichloroanthracene-1,2,3,4-tetrahydromide], colorless hexag. pr. from  $C_6H_6$ , m.p. 141-142° (3), while  $\bar{C}$  with  $Br_2$  vapor gives (3)  $\beta$ -[9,10-dichloroanthracene-1,2,3,4-tetrabromide], ndls. from  $C_6H_6$  (less sol. than  $\alpha$ -isomer), m.p. 178-179° (3), 178° (16) (8), 166° (15); both  $\alpha$ - and  $\beta$ -isomers with alc. KOH lose 2 HBr (the  $\alpha$ - more rapidly than the  $\beta$ -) yielding (3) (8) 2,3-dihromo-9,10-dichloroanthracene, yel. ndls., m.p. 255-256° (3), 251-252° (15) (16) (8).

[ $\bar{C}$  in  $CHCl_3$  treated with  $NO_2$  gas gives (26) 9,10-dichloro-9,10-dinitro-9,10-dihydroanthracene (very unstable white cryst. on strong cooling) which in boilg.  $CHCl_3$  yields anthraquinone (1:9095). —  $\bar{C}$  with conc.  $HNO_3$  ( $D = 1.43$ ) in AcOH at 15-18° yields (27) 9,10-dichloro-9-hydroxy-10-nitro-9,10-dihydroanthracene [Beil. VII<sub>1</sub>-(258)]]

[ $\bar{C}$  with fumg.  $H_2SO_4$  (20%  $SO_3$ ) in nitrobenzene at 12-15° (4) (5) cf. (28) (30) or in benzenesulfonyl chloride below 50° (28), or  $\bar{C}$  with  $ClSO_3H$  in  $CHCl_3$  or  $H_2SO_4$  nt 30° (29),

yields 9,10-dichloroanthracenesulfonic acid-2 [Beil. XI-(44)], cryst. with  $2\frac{1}{2}$  H<sub>2</sub>O from alc., m.p. 158-159° (4), losing aq. in vac. at 140° to anhydrous acid, m.p. 212° cor. dec. (4) (corresp. sulfonyl chloride, m.p. 221-225° dec., corresp. sulfonamide, m.p. 279°, corresp. sulfonanilide, m.p. 247.8° cor. (4)).] — [For disulfonation of  $\bar{C}$  see (33).]

$\bar{C}$  is unaffected (13) by boilg. alc. KOH. — [For behavior of  $\bar{C}$  with pyridine see (31). — For reactn. of  $\bar{C}$  with NaSH in alc. yielding anthranol, anthrone, dianthrone, and other prods. see (32). — For use of  $\bar{C}$  in prepn. of sulfur dyes see (34).]

$\bar{C}$  on oxidation yields (18) anthraquinone (1:9095).

$\bar{C}$  like many other anthracene derivs. adds to suitable unsatd. linkages (35) (36) (37) in Diels-Alder fashion: e.g.,  $\bar{C}$  with maleic anhydride (1.0625) in nitrobenzene, boiled for 15 min., gives on cooling (50% yield (35)) adduct, colorless pr. from xylene, m.p. 258-259°, from chlorobenzene, m.p. 253° (36); in this adduct the halogen is stable toward boilg. alc. KOH (38) (39), but the adduct with AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> refluxed 10 min. yields (35) 9,10-diphenylanthracene [Beil. V-747, V<sub>1</sub>-(377)], crystal from toluene, m.p. 248° (35). —  $\bar{C}$  with  $\beta$ -chloropropionic acid (3.0460) (used as source of acrylic acid (1:1020) by loss of HCl) boiled for 8 hrs. in o-dichlorobenzene yields an adduct, crystal from anisole, m.p. 245° (38); the halogen of this adduct is stable toward hydrolysis and is not removed by boilg. with 10% alc. KOH for 40 min. (38) —  $\bar{C}$  does not (38) form an adduct with cinnamic acid.

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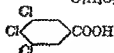
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### 3:4920 3,4,5-TRICHLOROBENZOIC ACID

C<sub>7</sub>H<sub>3</sub>O<sub>2</sub>Cl<sub>3</sub>

Beil. IX - 346

IX—



M.P. 210-210.5° (1)

203° (2)

Ndls. from aq. alc. — Sublimes in long ndls. — Somewhat volatile with steam. — Eas.



sol. cold alc., ether, acetone; mod. sol.  $C_6H_6$ ,  $CHCl_3$ ; spar. sol.  $CS_2$ , pet. eth.; alm. insol. cold aq.

[For prepn. of  $\bar{C}$  from 3,4,5-trichlorobenzaldehyde (3:2440) by oxidn. with alk.  $KMnO_4$  see (1); from 3,5-dinitro-4-aminobenzoic acid (chrysanic acid) [Beil. XIV-445] with fung.  $HCl$  at  $200^\circ$  see (2); for formn. (together with other products) from benzotrichloride (3:6540) +  $Cl_2$  see (3).]

[For study of  $Ag\bar{A}$ ,  $Ca\bar{A}_2 \cdot 6H_2O$ ,  $Ba\bar{A}_2 \cdot 4H_2O$  see (2).]

The direct nitration of  $\bar{C}$  has not been recorded. [However, 3,4,5-trichloro-2-nitrobenzoic acid, ndls. from alc., m.p.  $181-181.5^\circ$  (1), and 3,4,5-trichloro-2,6-dinitrobenzoic acid, m.p.  $219-221.5^\circ$  (1), have both been prepared from the corresponding aldehydes.]

$\bar{C}$  with  $PCl_5$  yields (2) 3,4,5-trichlorobenzoyl chloride, m.p.  $36^\circ$  (2).

— Methyl 3,4,6-trichlorobenzoate: unrecorded.

— Ethyl 3,4,5-trichlorobenzoate: from  $\bar{C}$  + alc. +  $HCl$  (2), ndls., m.p.  $86^\circ$  (2).

② 3,4,6-Trichlorobenzamide: from 3,4,5-trichlorobenzoyl chloride + conc. aq.  $NH_4OH$  at  $100^\circ$  (2); ndls. from  $C_6H_6$ , m.p.  $176^\circ$  (2).

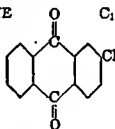
— 3,4,6-Trichlorobenzanilide: unrecorded.

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### 3:4922 2-CHLOROANTHRAQUINONE

 $C_{14}H_7O_2Cl$ 

Beil. VII - 787  
VII- (411)



M.P.  $212.4^\circ$  cor. (1)

$211.0^\circ$  cor. (2)

$210^\circ$  cor. (3)

$210^\circ$  (4)

$209^\circ$  (9)

$209.5^\circ$  (5) (6)

$208-209^\circ$  (7) (8)

M.P.  $208^\circ$  (36)

(Contd.)  $207^\circ$  (10) (11)

$206-207^\circ$  (12) (13)

$205-207^\circ$  (14)

$204.5-205.5^\circ$  (15)

$204^\circ$  (16) (18)

$203-204^\circ$  (17)

[See also 1-chloroanthraquinone (3:4480).]

Pale yel. ndls. from  $C_6H_6$ , chlorobenzene, or toluene; eas. sol. boilg.  $C_6H_6$ , toluene, or  $AcOH$ ; spar. sol. boilg. alc. — Sublimes in vac.

[For f.p./compn. data and diagram of system  $\bar{C}$  + 1-chloroanthraquinone (3:4480) (eutectic, m.p.  $143.9-144.2^\circ$ , contg. about 75%  $\bar{C}$ ) see (5).]

[For use of  $\bar{C}$  in coloring oils, fats, and waxes see (19);  $\bar{C}$  is widely used as intermediate in prepn. of many dyestuffs, but no general summary can be given here although selected examples occur in the following text.]

[For prepn. of  $\bar{C}$  from anthraquinonesulfonic acid-2 [Beil. XI-337, XI-(83)] or its Na salt with 25%  $HCl$  +  $NaClO_3$  at  $100^\circ$  (11) (20) (for use of this method in detn. of mixt. of anthraquinone- $\alpha$ - and  $\beta$ -sulfonic acids or their salts by f.p./compn. curve of resultant mixt. of 1-chloroanthraquinone (3:4480) +  $\bar{C}$  see (5)) see indic. refs.; from sodium anthraquinone-2-sulfonate in dil.  $HCl$  on exposure to light see (9), from anthraquinonesulfonic acid-2 on boilg. with dil.  $H_2SO_4$  +  $NaCl$  +  $NaClO_2$  see (21); from anthracenesulfonic

acid-2 [Beil. XI-194, XI<sub>1</sub>-(44)] with HCl + NaClO<sub>2</sub> at 100° see (22); from anthraquinone-sulfonic acid-2 or its Na salt (23) or from anthraquinonesulfonyl chloride-2 (24) with SOCl<sub>2</sub> in s.t. at 200-230° see indic. refs.]

[For prepn. of  $\bar{C}$  from  $\alpha$ -(4-chlorobenzoyl)benzoic acid [Beil. X-750, X<sub>1</sub>-(356)] by ring closure with conc. H<sub>2</sub>SO<sub>4</sub> at 160-170° (25) (16) (26) (27) (23) (4) (29) (34) (39) in pres. of AlCl<sub>3</sub> (30) see indic. refs. (for study of influence of conditions see espec. (27) (4) (31)); from  $\alpha$ -(3-chlorobenzoyl)benzoic acid (32) or from 2-benzoyl-4-chlorobenzoic acid [Beil. X-750, X<sub>1</sub>-(356)] (33) by similar ring closure with H<sub>2</sub>SO<sub>4</sub> see indic. refs.; from 4-chloro-2-benzoyl-benzoyl chloride on hgt. see (33).]

[For prepn. of  $\bar{C}$  from 2-chlorobutadiene-1,3 (chloroprene) (3:7080) + naphthoquinone-1,4 (1:9040) in C<sub>6</sub>H<sub>6</sub> see (6); from  $\alpha$ -chlorocrotonaldehyde (3:8117) + naphthoquinone-1,4 (1:9040) in C<sub>6</sub>H<sub>6</sub> with piperidine see (74); from 2-aminoanthraquinone (see below) via diazotization and rapid hgt. of diazonium chloride at 150° see (8); from 2-chloroanthraquinonecarboxylic acid-4 by hgt. at 256-290° (7) or from 2-chloroanthraquinonecarboxylic acid-5 by hgt. in s.t. at 310-320° or by distn. of its Ba salt with BaO see (17) of (15); from 2,9,10-trichloro-9-hydroxy-10-nitro-9,10-dihydroanthracene [Beil. VII<sub>1</sub>-(258)] in C<sub>6</sub>H<sub>6</sub>, nitrobenzene, or AcOH by hgt. at 90-95° see (35); from 2,9,10-trichloroanthracene [Beil. V<sub>1</sub>-(325)] (36) or from 2-chloroanthrone-9 (or 10) (12) by oxidn. with CrO<sub>3</sub> see indic. refs.]

[For prepn. of  $\bar{C}$  from 1-chloroanthraquinone (3:4480) by hgt. with conc. H<sub>2</sub>SO<sub>4</sub> at 200-205° for 9 hrs. see (37).]

[ $\bar{C}$  on reductn. with Zn dust + conc. aq. NH<sub>4</sub>OH under reflux yields (18) (37) 2-chloroanthracene [Beil. V<sub>1</sub>-(324)], m.p. 217° (37), 215° (18). —  $\bar{C}$  on reductn. with hydrazine hydrate in MeOH/KOH at 10 atm. and 135° for 1½ hrs. in pres. of Pd/CaCO<sub>3</sub> cat. yields (38) bis-(2,2'-anthraquinonyl) [Beil. VII<sub>1</sub>-(495)], m.p. 387-388°. —  $\bar{C}$  on reductn. with Al powder + conc. H<sub>2</sub>SO<sub>4</sub> (40) or with Sn + HCl (39) yields a mixt. of 3-chloroanthrone-9, m.p. 150° (38) (corresp. acetate, m.p. 146° (41) (42)), and 2-chloroanthracene-9, m.p. 155° (41) (corresp. acetate, m.p. 143° (41)); this mixt. of chloroanthrones can be sepd. by acetylation with Ac<sub>2</sub>O + pyridine and fractional crystn. of the resultant acetates (42). — For use of this reductn. method in prepn. of vat dyes see (43). — For study of oxidn./reductn. potential of  $\bar{C}$  see (13).]

[ $\bar{C}$  with MeOH/KOH in s.t. at 130° yields (44) 2-methoxyanthraquinone [Beil. VIII-343, VIII<sub>1</sub>-(658)], r.p. 196°. —  $\bar{C}$  with 2-hydroxyanthraquinone + NaOAc + Cu powder htd. at 250-260° for 12 hrs. gives (66% yield (45)) di-(2-anthraquinonyl) ether, pale yel. ndls. from pyridine, m.p. 324° (45). —  $\bar{C}$  with K xanthate + Cu powder boiled for 16 hrs. in AmOH gives (56% yield (45) (46)) di-(2-anthraquinonyl) sulfide, *cryst. from xylene*, m.p. 290.5-291° (45). —  $\bar{C}$  with thioacetic acid (2-mercaptobenzoic acid) + solid KOH htd. in AmOH at 150° for 8 hrs. gives (77% yield (3)) S-(2-anthraquinonyl)thioacetic acid [Beil. X<sub>1</sub>-(56)], m.p. 278° cor. (3); this prod. on hgt. with H<sub>2</sub>SO<sub>4</sub> or better with p-toluenesulfonyl chloride at 200° (3) (47) ring-closes by loss of H<sub>2</sub>O to 1,2-phthalylthioxanthone [Beil. XVII<sub>1</sub>-(291)], yel. ndls. from AcOH, m.p. 278° cor. (3).]

[ $\bar{C}$  with NaOH + glycerol htd. at 190° is claimed (48) to yield anthraquinone (1:9095). —  $\bar{C}$  with NaOH + NaClO<sub>2</sub> htd. 28 hrs. at 195° (49) cf. (50) (51) (52) gives (95% yield (49)) 1,2-dihydroxyanthraquinone (alizarin) (1:9165). —  $\bar{C}$  with NaSH boiled in aq. alc. yields (53) 2-mercaptoanthraquinone [Beil. VIII-346, VIII<sub>1</sub>-(659)], yel. ndls. from AcOH, m.p. 206° (54). —  $\bar{C}$  with Na<sub>2</sub>Se boiled in dil. alc. yields (55) 2-selenomercaptoanthraquinone, but  $\bar{C}$  with Se + NaOAc htd. at 205-210° in a mixt. of trichlorobenzene + tetralin for 8 hrs. yields (56) di-(2-anthraquinonyl) selenide.]

[ $\bar{C}$  with conc. aq. NH<sub>4</sub>OH in pres. of Cu salts under press. and at elevated temp. (180-200°) gives (yields: 97.5% (57), 98.6% (2)) (27) (58) (59) (60) 2-aminoanthraquinone [Beil. XIV-191, XIV<sub>1</sub>-(449)], red ndls., m.p. 302° (for study of influence of conditions see

(57) (2) (27) (61) (62)). —  $\bar{C}$  with hydrazine hydrate + pyridine in s.t. at 170° for 8 hrs. gives (20% yield (63)) 2-hydrazinoanthraquinone [Beil. XV<sub>1</sub>-(200)], or.-yel. ndls. from pyridine, m.p. 228-229° (63).]

[ $\bar{C}$  with 4 moles  $C_6H_5MgBr$  in ether yields (64) (65) 2-chloro-9,10-diphenylanthracene, yel. cryst. powder, or. ndls. from  $AcOH$ , m.p. 194° (64), 193° (66), 185° (65).]

[For formn. of addn. cpds. of  $\bar{C}$  with  $SbCl_5$  in  $CHCl_3$  see (10); for formn. of 2-anthraquinonylpyridinium chloride from  $\bar{C}$  +  $AlCl_3$  in pyridine see (67).]

[The direct sulfonation of  $\bar{C}$  appears not to have been reported in the scientific literature although  $\bar{C}$  with fuming  $H_2SO_4$  at 125-130° in pres. of Hg salts cf. (73) as directed is claimed in a patent (68) to yield 2-chloroanthraquinonesulfonic acid-5. — Two monosulfonic acids of  $\bar{C}$  are known, however, although prepared by indirect means; these are 2-chloroanthraquinonesulfonic acid-6 (corresp. sulfonyl chloride, deep yel. ndls. from chlorobenzene, m.p. 202° (69), from  $C_6H_6$ , m.p. 202-203° (71)), and 2-chloroanthraquinonesulfonic acid-7 (corresp. sulfonyl chloride, yel. cryst. from  $C_6H_6$ , m.p. 205° (70), 200-201° (71), 176° (69)); note that the alkali salts of both these acids are almost completely insoluble in aq. (71) and the above anomaly in m.p. of the sulfonyl chlorides may have been due to impure material. —  $\bar{C}$  on htg. with fuming  $H_2SO_4$  (40%  $SO_3$ ) at 180° yields (72) a mixt. of sulfonated products which on alk. fusion give 1,2,6-trihydroxyanthraquinone (flavopurpurin) [Beil. VIII-513, VII<sub>1</sub>-(741)] and 1,2,7-trihydroxyanthraquinone (anthrapurpurin) [Beil. VIII-516, VII<sub>1</sub>-(742)].]

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31, 1933; *Cent.* 1933, II 1764.

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1930, 1350. (43) Bayer and Co., *Ger.* 203,436, Oct. 20, 1908; *Cent.* 1908, II 1756. (44) Bayer and Co., *Ger.* 229,316, Dec. 13, 1910; *Cent.* 1911, I 180. (45) Perkin, Sewell, *J. Chem. Soc.* 123, 3036-3038 (1923). (46) Ullmann-Goldberg, *Ger.* 255,591, Jan. 10, 1913; *Cent.* 1913, I 480. (47) Ullmann, *Ger.* 238,983, Oct. 7, 1911; *Cent.* 1911, II 1289. (48) Oda, Tamura, Maeda,

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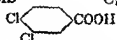
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## 3:4925 3,4-DICHLOROBENZOIC ACID

 $C_7H_4O_2Cl_2$ 

Beil. IX - 343

IX<sub>1</sub>-(141)

M.P. 211-212° (1)

208-209° (2) (20)

206° (3)

205° (4)

201-205° (5)

M.P. 204.1° (6)

(Contd.) 203° (7)

201-202° (8) (19)

201° (9)

200° cor. (10)

Ndls. from aq., alc., 60% alc. (6),  $C_6H_6$  (2) (6), or 30% AcOH (1) (18). — Volatile with steam. — Appreciably more sol. in hot aq. than in cold; very eas. sol. alc.

[For prepn. of  $\bar{C}$  from 3,4-dichlorotoluene (3:6355) by oxidn. (2) with  $CrO_3$  (8) (11), with dil.  $HNO_3$  in a.t. at 130-140° (9) (3), or with  $KMnO_4$  (6) see indic. refs.; for prepn. by oxidn. of 3,4-dichlorobenzyl chloride (8) (11), 3,4-dichlorobenzal chloride (3:6576) (5) (11), 3,4-dichlorobenzaldehyde (3:6559) (12), 3,4-dichlorobiphenyl (3:6685) (10), or chlorinated isopropylbenzene (cumene) (5) see indic. refs.; for prepn. from benzoic acid (1:0715) by actn. of  $HCl + KClO_3$  (11) (20) or  $Ca(OCl)_2$  (11) see indicated refs.; for still other mase. methods see Beil. IX-343 + IX<sub>1</sub>-(111)]

$\bar{C}$  is scarcely affected by litg. with fuming  $HNO_3$  (13) but on soln. in latter and treatment as directed (13) with conc.  $H_2SO_4$  yields 3,4-dichloro- $\alpha$ -nitrobenzoic acid, m.p. 160° (13). [This prod. may or may not be identical with that of m.p. 465° obtd. indirectly (14).]

$\bar{C}$  with  $PCl_5$  (15) or  $SOCl_2$  (16) yields 3,4-dichlorobenzoyl chloride, b.p. 242° (8), 159-160° at 42 mm. (15), 88.0-88.3° (16). [For formn. of this prod. in chlorination of  $BzCl$  see (4)]

— Methyl 3,4-dichlorobenzoate: unrecorded.

— Ethyl 3,4-dichlorobenzoate: b.p. 202-203° (5). [For study of rate of hydrolysis see (17)]

⑤ 3,4-Dichlorobenzamide: from 3,4-dichlorobenzoyl chloride +  $\text{NH}_3$  (8); m.p.  $133^\circ$  (8);  $166-168^\circ$  (17, 169° (18).

— 3,4-Dichlorobenzanilide: unrecorded.

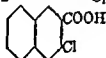
3:4925 (1) Cough, King, *J. Chem. Soc.* 1939, 690-691. (2) Kraay, *Rec. trav. chim.* 49, 1086 (1930). (3) Wynne, *J. Chem. Soc.* 1936, 705. (4) Hope, Reilly, *J. Chem. Soc.* 123, 2476 (1923). (5) Quist, Salo, *Acta Acad. Aboensis Math. et Phys.* 8, No. 4, 30 pp. (1934); *Cent.* 1934, 11 594-595; 1936, 1 538-540; *C.A.* 29, 6884 (1935). (6) Bornwater, Holleman, *Rec. trav. chim.* 31, 228-230 (1912). (7) Pieper, *Ann.* 142, 306 (1876). (8) Beilstein, Kuhlberg, *Ann.* 152, 224-224 (1869). (9) Lellmann, Klotz, *Ann.* 231, 313-314 (1885). (10) Scarborough, Waters, *J. Chem. Soc.* 1926, 560.

(11) Beilstein, *Ann.* 179, 283 (1875). (12) Gmelin, Bänziger, *Ber.* 29, 875 (1896). (13) Claus, Bücher, *Ber.* 29, 1624 (1887). (14) Ruggli, Zaeslin, *Helv. Chim. Acta* 19, 434-437 (1936). (15) Cohen, Briggs, *J. Chem. Soc.* 83, 1213 (1903). (16) Norris, Ware, *J. Am. Chem. Soc.* 61, 1418-1420 (1939). (17) Blakey, McCombie, Scarborough, *J. Chem. Soc.* 1926, 2863-2868. (18) Cohen, King, Strangeways, *J. Chem. Soc.* 1939, 3427. (19) Hodgson, Beard, *J. Chem. Soc.* 1927, 25. (20) Biswas, Das-Gupta, *J. Indian Chem. Soc.* 19, 497-498 (1912); *C.A.* 37, 5709 (1913).

### 3:4928 3-CHLORONAPHTHOIC ACID-2

 $\text{C}_{11}\text{H}_7\text{O}_2\text{Cl}$ 

Beil. IX - 661

IX<sub>1</sub>-(278)

M.P.  $216.5^\circ$  (1)

$216^\circ$  (2)

$212-213^\circ$  (3)

Cryst. from MeOH + aq. (2) or from  $\text{C}_6\text{H}_6$  (3). — Eas. sol. org. solv.

[For prepn. of  $\bar{\text{C}}$  from 3-aminonaphthoic acid-2 [Beil. XIV-535, XIV<sub>1</sub>-(623)] via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reactn. (alm. quant. yield) see (3); from the corresp. acid chloride (below) by hydrolysis with aq. see (1).]

$\bar{\text{C}}$  with Cu bronze refluxed in nitrobenzene for 2 hrs. gives (48% yield (4))  $\beta$ -naphthoic acid (1:0800), m.p.  $185^\circ$  (4).

[No record can be found of direct conv. of  $\bar{\text{C}}$  to the corresp. acid chloride (3-chloro-2-naphthoyl chloride); however, this compd., m.p.  $56.5^\circ$  (1), b.p.  $248^\circ$  at 160 mm. (1), has been ohtd. indirectly from 3-hydroxy-2-naphthoic acid (1:0850), with  $\text{PCl}_5$  in 49% yield (1); note that 3-hydroxy-2-naphthoic acid with  $\text{SOCl}_2$  gives instead 3-hydroxy-2-naphthoyl chloride, m.p.  $96^\circ$  (5),  $94.5^\circ$  (6), in 82% yield (5).

[For condens. of  $\bar{\text{C}}$  with pyrazolanthrone see (8).]

⑤ Methyl 3-chloro-2-naphthoate: cryst. from MeOH, m.p.  $58-59^\circ$  (3),  $58^\circ$  (7). [From  $\bar{\text{C}}$  in MeOH with conc.  $\text{H}_2\text{SO}_4$  (88% yield (7)), from  $\bar{\text{C}}$  with ethereal diazomethane (3), or from the acid chloride (above) with 5 pts. MeOH (3).] [For reactn. of this ester with 1-aminoanthraquinone see (7).]

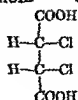
⑥ Ethyl 3-chloro-2-naphthoate: lfts. from lt. pet. or from alc., m.p.  $57-59^\circ$  (3),  $50^\circ$  (1); b.p.  $218-222^\circ$  at 160 mm. (1),  $195-197^\circ$  at 18 mm. (3), volatile with steam. [From  $\bar{\text{C}}$  in EtOH with HCl gas (1) (3).]

⑦ 3-Chloro-2-naphthoamide: ndls. from AcOH, m.p.  $236-237^\circ$  (1). [From the acid chloride (above) with conc. aq.  $\text{NH}_4\text{OH}$  (1).]

3:4928 (1) Scarborough, *Ann.* 31, 1158 (1913). (2) Hosaeus, *Ber.* 26, 668-671 (1893). (3) (4) Clemo, Spence, *J. Chem. Soc.* 1928, 2818. vs *Colourists* 56, 170 (1940). (6) Abrahart, *J. Ber.* 51, 22-23 (1918). (8) I.G., *Brit.* 298,775, Nov. 8, 1928; French 644,589, Oct. 10, 1928.

3:4930 *meso*- $\alpha,\alpha'$ -DICHLOROSUCCINIC ACID

Beil. II - 619

II<sub>1</sub>-(267)II<sub>2</sub>-(558)

M.P. 220° cor., dec. (in sealed cap. tube) (1)

217-218° (2)

214-218° (10)

215° u.c. (3)

215° dec. (4) (5) (6) (11) (18)

213° (7) (16)

210° dec. (8)

209-213° (9)

(See also *d,l*- $\alpha,\alpha'$ -dichlorosuccinic acid (3:4711).)

Hexag. pr. from aq. —  $\bar{C}$  is readily sol. aq. although less so than its *d,l*-isomer; e.g., 100 cc. satd. aq. soln. of  $\bar{C}$  at 0° conts. 12.0 g.  $\bar{C}$  (4);  $\bar{C}$  is eas. sol. alc., ether, acetone or  $\text{CHCl}_3$ ; spar. sol.  $\text{C}_6\text{H}_6$  or lgr.

[For prepn. of  $\bar{C}$  from disodium salt of maleic acid (1:0470) in satd. aq.  $\text{NaCl}$  soln. with  $\text{Cl}_2$  at 0° in dark or diffuse daylight (yields 74.5% (7), 66% (10), 65% (1)) cf. (10) see indic. refs. (note that as a side reactn. some addn. of  $\text{HOCl}$  also occurs leading to as much as 7% (1) chloromaleic acid); from fumaric acid (1:0895) with excess  $\text{Cl}_2$  in s.t. in sunlight for 3-4 days see (6); from *meso*- $\alpha,\alpha'$ -diaminosuccinic acid [Beil. IV-486, IV<sub>2</sub>-(901)] in aq.  $\text{HCl}$  with  $\text{NOCl}$  or  $\text{AgNO}_2$  (75% yield) see (3); from *meso*- $\alpha,\alpha'$ -dichlorosuccinyl (di)-chloride (3:0087) by hydrolysis with aq. see (5).]

[For formn. of  $\bar{C}$  from bis-acetyl peroxide (9) by decomposition in chloroacetic acid (3:1370) at 85-95° ( $\text{CO}_2 + \text{CH}_4$  are also formed) see (9).]

$\bar{C}$  behaves as a normal dibasic acid: titration with standard dil. aq. alk. gives Neut. Eq. 93.5. — [For study of acid strength ( $K_1 = 361 \times 10^{-4}$  at 20.2°,  $K_2 = 9.4 \times 10^{-4}$  at 17.8° (4)) see (4) (8); (18) for study of conductivity see (11).]

[Salts (of metals).  $\text{Ag}_2\bar{A}$ , amorphous ppt. (6) which on boilg with aq. for 10 hrs. yields (12) both *d,l*-tartaric acid (1:0550) and *meso*-tartaric acid (1:0490);  $\text{Ca}\bar{A} \cdot 2\text{H}_2\text{O}$ , eas. sol. aq. and alc. (6);  $\text{Sr}\bar{A} \cdot \text{H}_2\text{O}$  (6);  $\text{Ba}\bar{A}$ , very eas. sol. aq., insol. alc. (6);  $\text{Zn}\bar{A} \cdot 3\text{H}_2\text{O}$  (6);  $\text{Cd}\bar{A} \cdot 3\text{H}_2\text{O}$ , very eas. sol. aq., insol. alc. (6).]

$\bar{C}$  with cold aq.  $\text{KOH}$  loses 1  $\text{HCl}$  yielding (5) (7) (14) chlorofumaric acid (3:4853);  $\bar{C}$  with  $\text{NaOAc}/\text{AcOH}$  on boilg. (13) (17) or aq. soln. of  $\text{Na}_2\bar{A}$  on boilg.  $\frac{1}{2}$  hr. (12) loses 1  $\text{HCl}$  yielding chloromaleic acid (3:3432);  $\bar{C}$  on warming in dil.  $\text{H}_2\text{SO}_4$  gives both (14) chlorofumaric and chloromaleic acids. [For study of rate of decompn. of  $\bar{C}$  by aq., acids, or alkalis see (7) (8) (15).]

$\text{K}_2\bar{A}$  in aq. soln. maintained at neutrality at 100° dec. with formn. (14) of acetaldehyde (1:0100),  $\text{CO}_2 + \text{meso}$ -tartaric acid (1:0490).

$\bar{C}$  with  $\text{Ac}_2\text{O}$  at 150° yields (12) chloromaleic anhydride (3:0280).

The acid chloride (3:0087) corresp. to  $\bar{C}$  is known but is usually obtd. indirectly.

Ⓐ Dimethyl *meso*- $\alpha,\alpha'$ -dichlorosuccinate: m.p. 31.5-32° (see 3:0240).

Ⓑ Diethyl *meso*- $\alpha,\alpha'$ -dichlorosuccinate: m.p. 63° (see 3:1364).

— Acid salt of  $\bar{C}$  with *dl*, $\alpha$ -diphenylethylamine: tbls. from aq., m.p. 133-134° rap. htg. (13); satd. aq. soln. at 25° conts. 61.4 g./liter (13). [For the corresp. acid salts

of  $\bar{C}$  with the two opt. act. forms of this base see (13); both have m.p. 128–129°, and their satd. aq. solns. at 25° cont. 76.1 g./liter (13).]

3:4930 (1) Kuhn, Wagner-Jauregg, *Ber.* **61**, 501–502, 518–521 (1928). (2) Aminoff, *Arkiv Kemi, Mineral. Geol.* **7**, No. 9, 11 (1918); uhn, 928).  
 Zumstein, *Ber.* **59**, 485 (1926). (4) K -215  
 (5) Michael, Tissot, *J. prakt. Chem.* (2) (1894). (7) Robinson, Lewis, *J. Chem. Soc.* 1933, 1260–1262. (8) Holmberg, *J. prakt. Chem.* (2) **84**, 148, 152, 164 (1911). (9) Kharasch, Gladstone, *J. Am. Chem. Soc.* **65**, 17 (1943). (10) Terry, Eichelberger, *J. Am. Chem. Soc.* **47**, 1068, 1076–1077 (1925).  
 (11) Michael, Bunge, *Ber.* **41**, 2912 (1908). (12) Michael, Tissot, *J. prakt. Chem.* (2) **52**, 331–335 (1895). (13) van der Riet, *Ann.* **280**, 229 (1894). (14) Holmberg, *Arkiv Kemi, Mineral. Geol.* **8**, No. 2, 6, 32 (1920); *Cent.* 1921, I 830; *C.A.* **16**, 2116 (1922). (15) Johansson, *Z. physik. Chem.* **79**, 625–626 (1912). (16) Timmermans, van Laecker, Jaffe, *Bull. soc. chim. Belg.* **48**, 42 (1939). (17) Ashton, Partington, *Trans. Faraday Soc.* **30**, 602 (1934). (18) Holmberg, *Svensk. Kem. Tid.* **24**, 105–109 (1912); *Cent.* 1912, II 1618; *C.A.* **7**, 80 (1913).

3:4933 4-CHLORO-3-HYDROXYBENZOIC ACID  $C_7H_5O_3Cl$  Beil. S.N. 1068



M.P. 219.5–220.5° (1)

Colorless ndls. from aq.

[For prepn. of  $\bar{C}$  from 4-amino-3-hydroxybenzoic acid (1) via diazotization and use of  $Cu_2Cl_2$  reactn. see (1); note that the prod. formerly [Beil. X-143] supposed to have been  $\bar{C}$  is now regarded (1) as probably the 6-chloroisomer (3:4720).]

3:4933 (1) Beyer, *Rec. trav. chim.* **40**, 627 (1921).

3:4935 3,5-DICHLORO-2-HYDROXYBENZOIC ACID  $C_7H_4O_3Cl_2$  Beil. X - 104  
 (3,5-Dichlorosalicylic acid)  $X_1-(48)$



M.P. 220–221° (1)

219–220° (2)

219.5° (3) (10)

219° (4) (5) (6) (7)

215° (8)

214° (9) (11) (12)

Colorless scales or ndls. from aq. alc.; very spar. sol. hot aq., eas. sol. alc., ether; sublimes with partial decomposition.

[For prepn. of  $\bar{C}$  from o-hydroxybenzoic acid (salicylic acid) (1:0780) in aq. KOH (3 moles) (11) (10), or in aq. KOH (1 mole) (14) (17), or in aq. KOH (2 moles) (15) (16), in EtOH (17), in AcOH (12) (10) (2), or in  $CS_2$  susp. (17) with  $Cl_2$  see indic. refs.; with 30%  $H_2O_2 + HCl$  (80% yield) see (4); by htg. with  $SbCl_5$  see (13). (Note that by most of these methods 5-chloro-2-hydroxybenzoic acid (5-chlorosalicylic acid) (3:4705) may also be formed; from this  $\bar{C}$  may also be sep. via its spar. sol.  $Ba\bar{A}_2$  (17).)]

[For prepn. of  $\bar{C}$  from sulfosalicylic acid with  $Cl_2$  in aq. see (8); from K 2,4-dichlorophenolate with  $CO_2$  at 140° see (11); from 3,5-dichlorosalicylaldehyde by oxidn. with alk.

KMnO<sub>4</sub> (yield 100%) see {9}; from 3,5-dichloro-2-methoxybenzoic acid with 45% HI in s.t. at 120-130° see {3}; from chloral-3,5-dichlorosalicylamide by hydrolysis see {1}.]

$\bar{C}$  on htg. with CaO (17) {7} or at 200° in aniline (18) loses CO<sub>2</sub> yielding 2,4-dichlorophenol (3:0560).

$\bar{C}$  with FeCl<sub>3</sub> gives {13} {2} a dark violet color.

[ $\bar{C}$  in 60% fuming H<sub>2</sub>SO<sub>4</sub> treated with Cl<sub>2</sub> at 80-90° for 15 hrs. gives (70% yield {19}) 3,5,6-trichlorosalicylic acid, white pl. from aq. alc. or aq. AcOH, m.p. 207° cor. {19}; (this with Ac<sub>2</sub>O + trace H<sub>2</sub>SO<sub>4</sub> gives corresp. acetate, ndls. from lgr., m.p. 129.5° cor. {19}).]

$\bar{C}$  in AcOH treated with fuming HNO<sub>3</sub> yields {20} 4,6-dichloro-2-nitrophenol, m.p. 122° {20}.

$\bar{C}$  with PCl<sub>5</sub> (1 mole) yields (5) {10} 3,5-dichloro-2-hydroxybenzoylchloride (3,5-dichlorosalicyloyl chloride), ndls. from ether + pet. eth., m.p. 79°. [For details on various phosphorus compounds also formed in this reaction see {21}] [Note also existence of anhydride of  $\bar{C}$  (from the acid chloride + Ag $\bar{A}$ ), cryst. from CHCl<sub>3</sub>, m.p. 186-187° {5} {28}].

[ $\bar{C}$  in aq./alc./H<sub>2</sub>SO<sub>4</sub> gives {22} on electrolytic reduction 3,5-dichloro-2-hydroxybenzyl alcohol, ndls. from C<sub>6</sub>H<sub>6</sub>, m.p. 82° {22}; for study of prepn. and thermal rearr. of allyl {23}, crotyl {23}, benzyl {24}, and other {25} ethers of  $\bar{C}$  see indic. refs.]

① Methyl 3,5-dichloro-2-hydroxybenzoate: ndls. from alc. or ether, m.p. 150° {15}, 147° {5} {26}, 143-144° {7} {3}, 142° {12}. [From Ag $\bar{A}$  + MeI in s.t. at 135° {12}, from 3,5-dichlorosalicyloyl chloride (above) with MeOH {5}, or from methyl salicylate (1:1750) in AcOH with Cl<sub>2</sub> {26}]. [This ester with Ac<sub>2</sub>O yields {7} corresp. acetate, ndls. from MeOH, m.p. 57° {7}].

② Ethyl 3,5-dichloro-2-hydroxybenzoate: cryst. from ether, m.p. 57° {5}, 47° {12}. [From Ag $\bar{A}$  + C<sub>2</sub>H<sub>5</sub>I as above {12} {3}, from 3,5-dichlorosalicyloyl chloride (above) with EtOH {5}, or from ethyl salicylate (1:1755) with Cl<sub>2</sub> {27}].

— 3,5-Dichloro-2-hydroxybenzamide: m.p. 209° {11}.

— 3,5-Dichloro-2-hydroxybenzanilide: m.p. 134.5° {5} [From 3,5-dichlorosalicyloyl chloride (above) with aniline in ether {5}].

3:4935 {1} Hirwe, Rana, *Ber.* 72, 1353 (1939). {2} Hirwe, Rana, Gavankar, *Proc. Indian Acad. Sci. A-8*, 211 (1938). {3} Martini, *Gazz. chim. ital.* 29, II 62-63 (1899). {4} Leulier, Pinet, *Bull. soc. chim.* (4) 41, 1363-1364 (1927). {5} Anschütz, Mehring, *Ann.* 346, 300-311 (1906). {6} Biltz, Stepf, *Ber.* 37, 4030 (1904). {7} Zincke, *Ann.* 261, 252-254 (1891). {8} Datta, Mitter, *J. Am. Chem. Soc.* 41, 2037 (1919). {9} Dey, Row, *J. Chem. Soc.* 125, 560 (1924). {10} Earle, Jackson, *J. Am. Chem. Soc.* 28, 109 (1906).

{11} Tarugi, *Gazz. chim. ital.* 30, II 487-489 (1900). {12} Smith, *Ber.* 11, 1225-1227 (1878). {13} Lossner, *J. prakt. Chem.* (2) 13, 429-431 (1876). {14} Cahours, *Ann. chim.* (3) 13, 108-111 (1845); *Ann.* 52, 341-343 (1844). {15} Lasar-Cohn, Schultze, *Ber.* 38, 3300 (1905). {16} Ullmann, Kopetschn, *Ber.* 44, 428 (1911). {17} Hecht, *Am. Chem. J.* 12, 503-506 (1890). {18} Cazeneuve, *Bull. soc. chim.* (3) 15, 74 (1896). {19} Farnholt, Stuart, Twiss, *J. Am. Chem. Soc.* 62, 1239 (1940). {20} Smith, Kuerr, *Am. Chem. J.* 8, 93 (1886).

{21} Anschütz, *Ann.* 454, 81-82, 105-106 (1927). {22} Mettler, *Ber.* 39, 2939 (1906). {23} Tarbell, Wilson, *J. Am. Chem. Soc.* 64, 607-612 (1942). {24} Tarbell, Wystrach, *J. Am. Chem. Soc.* 65, 2146-2149 (1943). {25} Tarbell, Wystrach, *J. Am. Chem. Soc.* 65, 2149-2153 (1943). {26} Clausen, *Ann.* 418, 85 (1919). {27} Cahours, *Ann. chim.* (3) 27, 461-462 (1849); *Ann.* 74, 312 (1850). {28} Anschütz, *Ber.* 30, 223 (1897).

3:4936 4-CHLORONAPHTHOIC ACID-1



C<sub>11</sub>H<sub>7</sub>O<sub>2</sub>Cl Beil. IX - 651  
IX<sub>1</sub>—

M.P. 221-223° {2}  
210° {1}



Ndls. from alc.; eas. sol. alc. or AcOH; spar. sol. aq.,  $\text{CHCl}_3$ , ether, or hydrocarbons.

[For prepn. of  $\bar{C}$  from 4-aminonaphthoic acid-1 [Beil. XIV-533] by diazotization, conversion with  $\text{CuCN}$  to 4-chloronaphthonitrile (see below), and hydrolysis of the latter by boilg. with a mixt. of 50% AcOH (2 vols.) + conc.  $\text{H}_2\text{SO}_4$  (1 vol.) see (1); from 1-chloro-4-(chloromethyl)naphthalene, m.p. 78-79° (2), by oxidn. with dil.  $\text{HNO}_3$  see (2); or from 1-bromo-4-chloronaphthalene [Beil. V-548, V<sub>2</sub>-(445)] by conv. to  $\text{RMgBr}$  and carbonation see (2).]

$\bar{C}$  does not react either with conc.  $\text{NH}_4\text{OH}$  at 200° or with  $(\text{NH}_4)_2\text{CO}_3$  at 220° (1).

Salts. The alk. salts of  $\bar{C}$  are eas. sol. aq.; the calcium, barium, and silver salts are sparingly sol. aq.; the iron, lead, and copper salts are insol. aq. (1).

— Methyl 4-chloro-1-naphthoate: unreported.

— Ethyl 4-chloro-1-naphthoate: unreported.

— 4-Chloro-1-naphthonitrile: long white ndls. from AcOH, m.p. 110° (1).

① *p*-Bromophenacyl 4-chloro-1-naphthoate: m.p. 130.5-131° (2).

3:4936 (1) Friedländer, Weisberg, *Ber.* 23, 1840, 1842-1843 (1895). (2) Horn, Warren, *J. Chem. Soc.* 1946, 144.

3:4937 2,3,4,5,6-PENTACHLOROTOLUENE  
(*Eso*-Pentachlorotoluene)



$\text{C}_7\text{HCl}_5$  Beil. V - 303  
V<sub>1</sub>-(153)  
V<sub>2</sub>-(234)

M.P. 224.5-225.5° (1) B.P. 301° (5)  
224-224.5° (2)  
224° (3)  
218° (4) (5) (6) (7)  
217.5° u.c. (5)

White ndls. from  $\text{C}_6\text{H}_6$  or pet. eth. — Spar. sol. hot alc. or ether; spar. sol. cold  $\text{CS}_2$  but eas. sol. hot  $\text{CS}_2$ ; sol. at 17° in 22 vols. or at 87° in 3.4 vols. toluene (8). — Sublimes readily. — Closely resembles hexachlorobenzene (3:4939), and the m.p. of mixtures of the two are but very slightly depressed (7) (8); furthermore, soly. of  $\bar{C}$  in  $\text{C}_6\text{H}_6$  at 4 different temps. is alm. identical with that of hexachlorobenzene (9).

[For studies on dielectric characteristics of  $\bar{C}$  see (9) (10) (11) (12).]

[For prepn. of  $\bar{C}$  from toluene (1:7405) with  $\text{SO}_2\text{Cl}_2$  +  $\text{AlCl}_3$  +  $\text{S}_2\text{Cl}_2$  at 100° for  $\frac{1}{2}$  hr. as directed (72% yield (8)), or by electrolysis in AcOH/conc. HCl in dark (7), or with  $\text{Cl}_2$  in pres. of  $\text{I}_2$  followed by further chlorination in pres. of  $\text{SbCl}_3$  of the fraction boiling above 240° (6) see indic. refs.; for formn. of  $\bar{C}$  from isopropylbenzene (cumene) (1:7440) with  $\text{Cl}_2$  in pres. of  $\text{I}_2$  + Fe at 0°, or from *p*-cymene (1:7505) with  $\text{Cl}_2$  in pres. of  $\text{I}_2$  + Fe (1), or from 2-chlorotoluenesulfonyl chloride-1 with  $\text{Cl}_2$  in pres. of  $\text{SbCl}_3$  at 65-70° (4), or from 2,3,4-trichlorotoluene (3:0425) or 2,4,5-trichlorotoluene (3:2100) with  $\text{SO}_2\text{Cl}_2$  +  $\text{AlCl}_3$  +  $\text{S}_2\text{Cl}_2$  (8), or from 2,3,4-trichlorobenzal (di)chloride on stdg. (5) see indic. refs.]

[ $\bar{C}$  on further treatment with  $\text{SO}_2\text{Cl}_2$  +  $\text{AlCl}_3$  +  $\text{S}_2\text{Cl}_2$  gives (8) a prod. m.p. 272-274°. —  $\bar{C}$  on fusion and treatment with  $\text{Cl}_2$  at 210-230° as directed (13) gives 70-80% yield pentachlorobenzal (di)chloride (3:3590) b.p. 199° cor. at 13 mm. (13).]

[ $\bar{C}$  on partial hydrolysis with caustic alk. at 130-140° under press. yields (14) tetrachlororesol.]

$\bar{C}$  is unaffected by boilg. fung.  $\text{HNO}_3$  (6), but  $\bar{C}$  on oxidn. with 14.2 wt. p.a. conc.  $\text{HNO}_3$  (D = 1.42) in pres. of 0.1 pt. Hg by boilg. for 150 hrs. (5) yields pentachlorobenzoic acid (3:4910), m.p. 199.5° (5).

C.A. 32, 2548 (1938). (46) van der Linden, *Rec. trav. chim.* 57, 101ff, *Ber.* 18, 335-337 (1885). (48) Holleman, *Rec. trav. chim.*, *Rec. trav. chim.* 50, 787 (1931). (50) Istrati, *Bull. soc. chim.*

*m. Soc.* 68, 142 (1946); Dvornikoff (to Monsanto Chem. Co.), *A.* 30, 1394 (1936).

OIC ACID

 $C_7H_5O_2Cl$ 

Beil. IX - 340

IX<sub>1</sub>-(140)

	M.P.	
1) (2) (3) (4) (64)	238-239°	(23) (70)
(5)	238°	(24)
(6) (7)	237°	(66) (133)
(8)	236-237°	(25) (126)
(9) (10)	236.5°	(67)
(11) (12)	236°	(26) (27) (28) (29)
(13)		(51) (54) (61) (72)
(14) (15) (16) (17)		(77) (86) (156)
(18) (39) (40)	235.5-236°	(30)
(19)	235-236°	(55)
(20)	235.5°	(31) (53)
(21) (22)	235°	(32) (33) (34) (36)
	234-235°	(56) (71)
	234°	(50)
	233-234°	(69)

—  $\bar{C}$  is almost insol. in cold aq.; e.g., 100 ml. satd. aq. soln. at 25° conts. note that  $\bar{C}$  is thus much less sol. in aq. than *m*-chlorobenzoic acid (3:4392) than *o*-chlorobenzoic acid (3:4150). — At 14-16° 100 ml. satd. soln. of  $\bar{C}$  2.6 g.  $\bar{C}$ , in EtOAc 1.6 g.  $\bar{C}$ , in 75% AcOH 0.3 g.  $\bar{C}$ , in  $CCl_4$  0.04 g.  $\bar{C}$ , in  $CS_2$  0.16 g.  $\bar{C}$  (22). — [For study of soly. of  $\bar{C}$  in acetone (8),  $C_6H_6$  (9) see indic. refs.]

distribution at 25° of  $\bar{C}$  between aq. + toluene or aq. +  $CHCl_3$  see (35); of  $\bar{C}$  on charcoal from its solns. in acetone or  $C_6H_6$  see (5); for soly. of  $\bar{C}$  in various salts (including NaA) see (33).]

blimed in vac. (19). —  $\bar{C}$  is but very slightly volatile with steam (for details [For crystallographic data see (36) (37).]

tems contg.  $\bar{C}$ . [For f.p./compn. data on system  $\bar{C}$  + aq. see (38). — For data and diagrams of system  $\bar{C}$  +  $BzOH$  (1:0715), eutectic, m.p. 115°, contg. %  $\bar{C}$ , see (22) (16); for f.p./compn. data on systems  $\bar{C}$  + *p*-toluic acid (1:0795) *p*-hydroxybenzoic acid (1:0840) (11), or  $\bar{C}$  + *p*-methoxybenzoic acid (anisic (35) (15) see indic. refs.]

/compn data and diagrams on systems  $\bar{C}$  + *o*-chlorobenzoic acid (3:4150), a.p. 132°, contg. abt. 14 mole %  $\bar{C}$ , see (22) (39); on system  $\bar{C}$  + *m*-chlorobenzoic 392), eutectic, m.p. 140.9°, contg. 20 mole %  $\bar{C}$  (22) (39) (40), see indic. refs.]

*p*/compn data and diagrams on systems  $\bar{C}$  + *m*-bromobenzoic acid (16),  $\bar{C}$  + benzoic acid (16),  $\bar{C}$  + *p*-nitrobenzoic acid (41),  $\bar{C}$  + *p*-iodobenzoic acid (42) :: refs.]

ary systems contg.  $\bar{C}$ . [For influence of addn. of  $\bar{C}$  to the eutectic mixt. of *o*-benzoic acid (3:4150) with *m*-chlorobenzoic acid (3:4392) see (43); for data on y system of all three chlorobenzoic acids, eutectic m.p. 104.9°, contg. 48.3 mole % + 44.0 mole % *meta* + 7.7 mole % *para* isomers, see (39).]

+  $\text{Cl}_2$  + anhyd.  $\text{FeCl}_3$  at  $125^\circ$  (33), cf. (34); from various addn. prods. of chlorine with trichloro- (35), tetrachloro- (36), or pentachloro- (37) benzenes usually by means of  $\text{MeOH}/\text{NaOH}$ , from 2,3,5,6-tetrachloro-*N*-nitroaniline, 2,3,5,6-tetrachloro-*N*-nitroacetanilide, or 2,3,5,6-tetrachloro-4-nitro-*N*-nitroaniline in boilg.  $\text{AcOH}$  + conc.  $\text{HCl}$  (8), from tetrachlorophthalyl *sym*-dichloride or from pentachlorobenzoyl chloride on distn. (38).]

$\bar{\text{C}}$  with  $\text{H}_2$  over  $\text{Ni}$  at  $270^\circ$  gives (39)  $\text{C}_6\text{H}_6$ , chlorobenzene, dichlorobenzene, trichlorobenzene, etc. —  $\bar{\text{C}}$  in boilg. alc. with large excess of  $\text{Na}$  is completely dehalogenated (40).

$\bar{\text{C}}$  is unattacked by  $\text{ICl}$  in s.t. at  $300^\circ$  (41) and does not react with  $\text{MeMgI}$  or with  $\text{MeMgBr}$  in ether even on long boilg. (42).

[ $\bar{\text{C}}$  with liq.  $\text{Cl}_2$  in sunlight yields (37) by addn. both decachlorocyclohexane, m.p.  $92^\circ$ , and dodecachlorocyclohexane, m.p. in sealed cap. tube  $285^\circ$ . —  $\bar{\text{C}}$  with  $\text{F}_2$  in  $\text{CCl}_4$  soln. at  $0^\circ$  yields (43) small amts. of both hexachlorotetrafluorocyclohexene,  $\text{C}_6\text{Cl}_4\text{F}_2$ , m.p.  $113$ – $114^\circ$ , and hexachlorohexafluorocyclohexane,  $\text{C}_6\text{Cl}_2\text{F}_4$ , m.p.  $94$ – $96^\circ$ . —  $\bar{\text{C}}$  in vapor phase with  $\text{F}_2$  in pres. of  $\text{Cu}$  gives a mixt. of 12 individual prods. (44).]

$\bar{\text{C}}$  with aq.  $\text{NaOH}$  at  $135$ – $138^\circ$  and 11–12 atm. for 3–4 hrs. (14) or with excess 5–15% soln. of  $\text{NaOH}$  in  $\text{MeOH}$  at  $135^\circ$  under press. (45) or  $\bar{\text{C}}$  with  $\text{NaOH}$  in  $\text{EtOH}$  in s.t. at  $150$ – $160^\circ$  (47) or in dry glycerol at  $250$ – $280^\circ$  (47) gives (80% yield (14)) sodium salt of pentachlorophenol (3:4850). —  $\bar{\text{C}}$  with  $\text{MeOH}/\text{NaOH}$  in ethyl methyl ketone soln. at b.p. for  $\frac{1}{2}$  hr. gives (43% yield (46)) methyl pentachlorophenyl ether, ndls. from alc., m.p.  $108$ – $109^\circ$ . [For studies of kinetics of reactn. of  $\bar{\text{C}}$  with  $\text{MeOH}/\text{NaOH}$  in s.t. at  $151^\circ$  (2), at  $176^\circ$  (48), at  $180^\circ$  (48), at  $183^\circ$  (49) see indic. refs.; of  $\bar{\text{C}}$  with  $\text{EtOH}/\text{NaOH}$  or with  $\text{NaOEt}$  soln. at  $175^\circ$  see (2).]

$\bar{\text{C}}$  on boilg. with mixt. of fuming  $\text{HNO}_3$  + conc.  $\text{H}_2\text{SO}_4$  gives (50) tetrachlorobenzoquinone-1,4 (chloranil) (3:4978).

- (1941). (10) Smyth, Lewis, *J. Am. Chem. Soc.* **63**, 950 (1940).  
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 (31) Consortium für Elektrochem. Ind., French **814,423**, June 23, 1937; *Cent.* **1937**, II 3953. (32) I.G., French **837,741**, Feb. 20, 1939; *Cent.* **1939**, II 228. (33) Fierz-David, Stäbelin, *Helv. Chim. Acta* **20**, 1458–1461 (1937). (34) van der Linden, *Rec. trav. chim.* **57**, 342–344 (1938). (35) van der Linden, *Rec. trav. chim.* **55**, 317–320 (1936). (36) van der Linden, *Rec. trav. chim.* **55**, 421–430 (1936). (37) van der Linden, *Rec. trav. chim.* **55**, 569–573 (1936). (38) Kirpal, Kunze, *Ber.* **62**, 2104–2105 (1929). (39) Mailhe, *Cent.* **1921**, III 467. (40) Stepanov, *J. Russ. Phys.-Chem. Soc.* **37**, 15 (1905); *Cent.* **1905**, I 1273.  
 (41) Krafft, Merz, *Ber.* **8**, 1303 (1875). (42) Durand, Hsün, *Compt. rend.* **191**, 1460 (1930). (43) Bigelow, Pearson, *J. Am. Chem. Soc.* **56**, 2773–2774 (1934). (44) Fukuhara, Bigelow, *J. Am. Chem. Soc.* **60**, 427–429 (1938). (45) Smith, Litvak (to Dow Chem. Co.), U.S. **2,107,650**,

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(51) Dvornikoff, *J. Am. Chem. Soc.* 68, 142 (1946); Dvornikoff (to Monsanto Chem. Co.), U. S. 2,028,383, Jan. 21, 1936; *C.A.* 30, 1394 (1936).

### 3:4940 *p*-CHLOROBENZOIC ACID

 $C_7H_5O_2Cl$ 

Beil. IX - 340

IX<sub>1</sub>-(140)

M.P.	[246° (160)]	M.P.	238-239° (23) (70)
243°	(1) (2) (3) (4) (64)	(Contd.) 238°	(24)
243° in a.t.	(5)	237°	(66) (133)
242.5-243.5°	(6) (7)	236-237°	(25) (126)
241.7°	(8)	236.5°	(67)
241.5°	(9) (10)	236°	(26) (27) (28) (29)
241°	(11) (12)		(51) (54) (61) (72)
240-241°	(13)		(77) (86) (156)
240°	(14) (15) (16) (17)	235.5-236°	(30)
	(18) (38) (40)	235-236°	(55)
239.7°	(19)	235.5°	(31) (53)
239° cor.	(20)	235°	(32) (33) (34) (36)
239°	(21) (22)	234-235°	(56) (71)
		234°	(50)
		233-234°	(69)

Cryst. from alc. —  $\bar{C}$  is almost insol. in cold aq.; e.g., 100 ml. satd. aq. soln. at 25° conts. 0.0068 g.  $\bar{C}$  (33); note that  $\bar{C}$  is thus much less sol. in aq. than *m*-chlorobenzoic acid (3:4392) and far less sol. than *o*-chlorobenzoic acid (3:4150). — At 14-16° 100 ml. satd. soln. of  $\bar{C}$  in acetone conts. 2.6 g.  $\bar{C}$ , in EtOAc 1.6 g.  $\bar{C}$ , in 75% AcOH 0.3 g.  $\bar{C}$ , in  $CCl_4$  0.04 g.  $\bar{C}$ , in  $C_6H_6$  0.017 g.  $\bar{C}$ , in  $CS_2$  0.16 g.  $\bar{C}$  (22). — [For study of soly. of  $\bar{C}$  in acetone (8),  $C_6H_6$  (8) (9), heptane (9) see indic. refs.]

[For study of distribution at 25° of  $\bar{C}$  between aq. + toluene or aq. +  $CHCl_3$  see (35); for adsorption of  $\bar{C}$  on charcoal from its solns. in acetone or  $C_6H_6$  see (8); for soly. of  $\bar{C}$  in aq. solns. of various salts (including NaA) see (33).]

$\bar{C}$  can be sublimed in vac. (19). —  $\bar{C}$  is but very slightly volatile with steam (for details see (10)). — [For crystallographic data see (36) (37).]

Binary systems contg.  $\bar{C}$ . [For f.p./compn. data on system  $\bar{C}$  + aq. see (38). — For f.p./compn. data and diagrams of system  $\bar{C}$  + BrOH (1:0715), eutectic, m.p. 115°, contg. about 10 wt %  $\bar{C}$ , see (22) (16); for f.p./compn. data on systems  $\bar{C}$  + *p*-toluic acid (1:0795) (11),  $\bar{C}$  + *p*-hydroxybenzoic acid (1:0840) (11), or  $\bar{C}$  + *p*-methoxybenzoic acid (anisic acid) (1:0805) (15) see indic. refs.]

[For f.p./compn. data and diagrams on systems  $\bar{C}$  + *o*-chlorobenzoic acid (3:4150), eutectic, m.p. 132°, contg. abt. 10 wt %  $\bar{C}$ , see (22) (16);  $\bar{C}$  + *m*-chlorobenzoic acid (3:4392), eutectic, m.p. 132°, contg. abt. 10 wt %  $\bar{C}$ , see (22) (16);  $\bar{C}$  + *p*-chlorobenzoic acid (3:4392), eutectic, m.p. 132°, contg. abt. 10 wt %  $\bar{C}$ , see (22) (16);  $\bar{C}$  + *p*-iodobenzoic acid (42) see indic. refs.]

[For f.p./compn. data and diagrams on systems  $\bar{C}$  + *p*-bromobenzoic acid (16),  $\bar{C}$  + *p*-iodobenzoic acid (42) see indic. refs.]

Ternary systems contg.  $\bar{C}$ . [For influence of addn. of  $\bar{C}$  to the eutectic mixt. of *o*-chlorobenzoic acid (3:4150) with *m*-chlorobenzoic acid (3:4392) see (43); for data on ternary system of all three chlorobenzoic acids, eutectic m.p. 104.9°, contg. 48.3 mole % *ortho* + 44.0 mole % *meta* + 7.7 mole % *para* isomers, see (39).]

Miscellaneous. [For study of fate of  $\bar{C}$  in animal organism see (44) (45) (46) (47); note that conjugation with glycine to yield the expected *N*-(*p*-chlorobenzoyl)glycine (*p*-chlorohippuric acid) [Beil. IX-341], m.p. 143° (45), does occur. — For study of toxicology of  $\bar{C}$  see (46) (48). — Note that sodium salt of  $\bar{C}$  (see also below) is widely used under name "Mikrobin" as preservative. — For use of  $\bar{C}$  as vulcanization regulator see (49).]

Preparation. [For prepn. of  $\bar{C}$  from *p*-chlorotoluene (3:8287) by oxidn. with boilg. 5% aq.  $KMnO_4$  (60% yield (51)) (22) (50) (52) (53) (133), with  $MnO_2 + H_2SO_4$  (100% yield (51)), with  $CrO_3$  (54), with dil.  $HNO_3$  in s.t. at 140–145° for  $\frac{1}{2}$  hr. (55) or at 115–120° for 5–6 hrs. (56) see indic. refs.; from *p*-chlorotoluene (3:8287) by oxidn. with air in the pres. of various catalysts (57), or at 235–240° and 50–60 atm. press. in pres. of  $FeO \cdot OH$  (58), or in aq. alk. at 260° under press. (59) see indic. refs.; for formn. of  $\bar{C}$  from *p*-chlorotoluene (3:8287) by electrolytic oxidn. (2) (60), by action of  $NOCl$  (30), or by long exposure to  $I_2 + aq.$  in light (28) see indic. refs.]

[For prepn. of  $\bar{C}$  from *p*-chloroacetophenone (3:6735) by oxidn. with alk.  $KMnO_4$  (61), with  $CrO_3/AcOH/H_2SO_4$  (95% yield (71)), with  $Cl_2 + NaOH$  ( $NaOCl$ ) in nq.  $MeOH$  (93% yield (62)), by liquid phase cat. oxidn. with air in pres. of  $MnO_2$  (91% yield (6)) see indic. refs.; for formn. of  $\bar{C}$  from *p*-chloroacetophenone (3:6735) with  $NOCl$  see (63).]

[For formn. of  $\bar{C}$  from 4-chloro-isopropylbenzene (*p*-chlorocumene) (3:8705) by oxidn. with  $HNO_3$  (64) (23), from 2,4'-dichlorobiphenyl (3:0670) (65) or from 4,4'-dichlorobiphenyl (3:4300) (66) by oxidn. with  $CrO_3/AcOH$ , from benzal-4-chloroacetophenone (24) by oxidn. with  $KMnO_4$  in pyridine (90% yield (24)) see indic. refs.]

[For formn. of  $\bar{C}$  from *p*-chlorobenzaldehyde (3:0765) by oxidn. with  $KMnO_4$  (67) (68) (69) (70) or  $CrO_3$  (67) or even slowly by air see indic. refs.; from *p*-chlorobenzaldehyde copper during recrystn. (presumably as a result of oxidn. by air) see (31).]

[For prepn. of  $\bar{C}$  from *p*-chlorobenzonitrile [Beil. IX-341, IX-1(140)] by hydrolysis with 75%  $H_2SO_4$  (71), from *p*-chlorobenzoyl chloride (3:6550) by hydrolysis with nq., from *p*-chlorobenzotrichloride (3:6825) by hydrolysis, e.g., with aq. in s.t. at 200° (72) or with aq. alk., alk. carbonates, or alk.-carb carbonates (73) (note also formn. of  $\bar{C}$  as by-prod. of prepn. of *o*-chlorobenzaldehyde from *o*-chlorotoluene presumably due to hydrolysis of some *p*-chlorobenzotrichloride (81)), from *p*-chlorobenzal (di)chloride (3:6700) with  $CrO_3$  (74) or on boilg. with aq. for 20 hrs. followed by oxidn. with  $KMnO_4$  (85% yield (17)); from a mixt. of *p*-chlorobenzotrichloride + *p*-chlorobenzal (di)chloride by bydral. with 70%  $H_2SO_4$  or 80%  $AcOH$  or 5%  $NaOH$  at 90–100° in stream of air to effect immediate oxidn. (75) see indic. refs.]

[For prepn. of  $\bar{C}$  from 2-(*p*-chlorobenzoyl)benzoic acid [Beil. X-750, X-1(356)] by hydrolytic cleavage with nq. +  $CaO$  under press. at 325° (93% yield (7)), or from *p*-chlorobromobenzene via conversion to *p*-chlorophenyl lithium bromide (76) or to *p*-chlorophenyl magnesium bromide (77) and subsequent carbonation (90% yield (76)) or from chlorobenzene (3:7903) with  $AlCl_3 + CO_2$  at 100° and 60 atm. press. (82) see indic. refs.]

[For formn. of  $\bar{C}$  from benzoic acid (1:0715) with alk.  $NaOCl$  (20) cf. (78) or  $Ca(OCl)_2$  (79) cf. (25), or from 4-chlorophthalic acid (3:4390) by cat. monodecarboxylation (80), see indic. refs.]

[For formn. of  $\bar{C}$  from di-(*p*-chlorobenzoyl) peroxide by htg. (2) (3), from *p*-aminobenzoic acid via diazotization and use of  $Cu_2Cl_2$  reaction (82% yield (83)), from *p,p'*-diazoaminobenzoic acid (diazoaminobenzene-4,4'-dicarboxylic acid) [Beil. XVI-728] with conc.  $HCl$  (84), from *p*-chloroisooctroacetophenone with warm  $Ac_2O$  (21), from *p*-chlorophenacyl bromide by conv. to quaternary salt with quinoline and treatment with aq.  $NaOH$  (18), from *p*-borobenzoic acid with hot nq.  $CuCl_2$  (26), from di-(*p*-chlorobenzoyl)butane on pyrolysis at 255–265° for 24 hrs. (85), from ethyl *p*-chlorophenyl-azo-carboxylate during oxidn. with  $H_2O_2$  in  $AcOH$  (29), from *p*-hydroxybenzoic acid (1:0840) with  $PCl_5$  followed by aq. (86) (87), or from treatment with nq. of the product from *p*-nitrotoluene with

$\text{SOCl}_2$  in s.t. at 200–220° (88), *p*-toluenesulfonyl chloride with  $\text{SOCl}_2$  in s.t. at 230–250° (88), or sodium *p*-toluenesulfonate in chlorobenzene with  $\text{SOCl}_2$  in s.t. at 250–260° (89) see indic. refs.]

**Chemical behavior.** No specific account of reduction of  $\tilde{\text{C}}$  to benzoic acid appears to be on record; note, however, detn. of chlorine in  $\tilde{\text{C}}$  by use of  $\text{Na} + \text{alc.}$  (90). —  $\tilde{\text{C}}$  on reduction with formic acid at 250–260° in pres. of  $\text{TiO}_2$  gives *p*-chlorobenzaldehyde (3:0765) (89% yield on  $\tilde{\text{C}}$  consumed, or 41% on  $\tilde{\text{C}}$  used (91)). —  $\tilde{\text{C}}$  on electrolytic reduction in alc /  $\text{H}_2\text{SO}_4$  gives (92) *p*-chlorobenzyl alcohol [Beil. VI-444, VI-1-(222)], m.p. 73°, h.p. 234° (92); note proximity of m.p. of this prod. to that (72°) of corresp. prod. obtd. by similar reduction of *o*-chlorobenzoic acid (3:4150). — For study of reduction of  $\tilde{\text{C}}$  with  $\text{H}_2 + \text{Ni}$  in aq. alk. at ord. temp. see (93).

[ $\tilde{\text{C}}$  on electrolytic oxidn. in  $\text{AcOH}/\text{H}_2\text{SO}_4$  gives (2) 4-chloro-2-hydroxybenzoic acid (4-chlorosalicylic acid) (3:4903).]

$\tilde{\text{C}}$  behaves normally as a monobasic acid; e.g.,  $\tilde{\text{C}}$  on titration with standard dil. aq. alk. gives Neut. Eq. 156.5; ionization constant at 25° is  $0.93 \times 10^{-4}$  (94),  $0.78 \times 10^{-4}$  (95),  $1.04 \times 10^{-4}$  (96) cf. (97) (12). — [For study of acid strength of  $\tilde{\text{C}}$  in various alcohols see (98) (99) (100) (13) (101) (27).] — For soly. of  $\tilde{\text{C}}$  in aq. solns. of various salts (including  $\text{Na}\tilde{\text{A}}$ ) see (33). — For sepn. of  $\tilde{\text{C}}$  from *o*-chlorobenzoic acid (3:4150) by use of difference in acid strength see (102).]

**Salts of inorganic bases.**  $\text{NH}_4\tilde{\text{A}}$  (103). — Hydroxylamine salt; m.p. 130° (104). —  $\text{Na}\tilde{\text{A}}$ : widely used as food preservative under name "Mikrobin"; for prepn. from  $\tilde{\text{C}}$  + Na phenolate see (105); for study of influence on enzymes see (106) (107); for study of use as preservative see (108); for studies of detection and/or detn. in foods see (109) (110) (111) (112) (113) (114); forms liquid cryst. on fusion (115).

$\text{Ag}\tilde{\text{A}}$ , sol. in hot aq. (50) (1 l. satd. aq. soln. at 20° conts. 1.08 g. (118)). (Note that this salt (1 mole) with  $\text{I}_2$  (2 equivalents) in dry  $\text{C}_6\text{H}_6$  refluxed 15–18 hrs. yields (116) phenyl *p*-chlorobenzoate, m.p. 100° +  $\text{CO}_2$  +  $\text{AgI}$ , and that analogous behavior is shown to lesser degree by corresp. salt of *m*-chlorobenzoic acid (3:4392) but not by corresp. salt of *o*-chlorobenzoic acid (3:4150).)

$\text{Ca}\tilde{\text{A}}_2 \cdot 3\text{H}_2\text{O}$  (25), 1 l. satd. aq. soln. at 20° conts. 7.37 g. (118). —  $\text{Ba}\tilde{\text{A}}_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$  (66);  $\text{Ba}\tilde{\text{A}}_2 \cdot 4\text{H}_2\text{O}$  (34);  $\text{Ba}\tilde{\text{A}}_2 \cdot \text{H}_2\text{O}$  (118); 1 l. satd. aq. soln. of latter at 20° conts. 1.09 g.  $\text{Ba}\tilde{\text{A}}_2 \cdot \text{H}_2\text{O}$  (118) (for use of Ba salt in sepn. of the three isomeric chlorobenzoic acids see (43)). —  $\text{Cd}\tilde{\text{A}}_2 \cdot 2\text{H}_2\text{O}$  (117); 1 l. satd. aq. soln. at 20° conts. 7.79 g. (118). — For similar data on salts of  $\tilde{\text{C}}$  with other heavy metals see (118) (119). — For study of various metal ions as precipitants for  $\tilde{\text{C}}$  see (120).

**Salts of organic bases.**  $\tilde{\text{C}}$  with equiv. amt. benzylamine in boilg.  $\text{EtOAc}$  followed by evapn. of solvent yields (121) benzylammonium *p*-chlorobenzoate, m.p. 157.4–158.4° u.e., 160.3–161.3° cor., Neut. Eq. 263.6. —  $\tilde{\text{C}}$  similarly treated with  $\alpha$ -phenylethylamine yields (121)  $\alpha$ -phenylethylammonium *p*-chlorobenzoate, m.p. 150.0–151.0° u.e., 152.2–153.2° cor., Neut. Eq. 277.6.

$\tilde{\text{C}}$  (1 mole) in alc. mixed with codeine (1 mole), m.p. 155°, htd. several minutes, solvent evapd. and resultant sirup recrystd. from aq., yields (122) codeine *p*-chlorobenzoate,  $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}_2\tilde{\text{C}}$ , m.p. 162° on "Maquenne block"; note that this value although close to that (166°) of codeine *p*-bromobenzoate is widely different from and higher than those for the corresp. salts of either *o*-chlorobenzoic acid (3:4150) or *m*-chlorobenzoic acid (3:4392) which are 134° and 96° respectively. —  $\tilde{\text{C}}$  (1 mole) in alc. (or  $\text{CHCl}_3$ ) with strychnine (1 mole) in alc., boiled for a few minutes, then cooled, yields (123) strychnine *p*-chlorobenzoate,  $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2\tilde{\text{C}}$ , m.p. 251° on "Maquenne block"; note that the m.p. of this salt is far higher than the corresp. products from similar treatment of either the *o*- or *m*-isomers, which are 170° and 185°, respectively.

$\tilde{\text{C}}$  with alcohols gives by conventional processes the corresp. esters: for details on methyl

*p*-chlorobenzoate (3:0535) or on ethyl *p*-chlorobenzoate (3:6750) see these compds. — [For study of rate of esterification of  $\bar{C}$  with MeOH (124) (125) (126), with EtOH (126) (1) (127), with cyclohexanol (128) see indic. refs.]

$\bar{C}$  with oxalyl (di)chloride (3:5060) refluxed in  $C_6H_6$  (129), or Na $\bar{A}$  htd. with *p*-chlorobenzoyl chloride (3:6550) (130) gives (50% yield (130)) *p*-chlorobenzoic acid anhydride, ndls. from dil. acetone or  $C_6H_6$ , m.p. 193–194° (129) (131), 194.8° (130), 191.5° (132); note that this prod. may also form in various other reactions involving  $\bar{C}$ , especially in pres. of tertiary bases or  $Na_2CO_3$  cf. (131) (132).

$\bar{C}$  with  $PCl_5$  (133) (50) (45) (132), with  $SOCl_2$  (134) (135) (136), with  $SOCl_2 + AlCl_3$  (137), or with *p*-chlorobenzotrichloride (3:6825) +  $ZnCl_2$  (138) gives *p*-chlorobenzoyl chloride (3:6550).

[ $\bar{C}$  with chlorobenzene (3:7903) +  $AlCl_3$  refluxed 5½ hrs. gives (98% yield (7)) a mixt. consisting mainly of 4,4'-dichlorobenzophenone (3:4270) accompanied by a small proportion of 2,4'-dichlorobenzophenone (3:1565).]

[ $\bar{C}$  with KCN + CuCN in aq. alc. btd. in s.t. at elevated temp. (139) or  $\bar{C}$  (as K $\bar{A}$ ) with aq. KCN + CuCN refluxed 8–10 hrs. under  $H_2$  in quartz flask exposed to ultra-violet light (140) gives (70% yield (140)) terephthalic acid (1:0910).]

Substitution of nucleus of  $\bar{C}$ .  $\bar{C}$  on mononitration, e.g., with  $HNO_3$  ( $D = 1.6$ ) on warming until soln. occurs (141), or with 10 wt. pts.  $HNO_3$  ( $D = 1.5$ ) at 55–60° for 10 minutes (142), or with 4 vols.  $HNO_3$  ( $D = 1.5$ ) warmed until soln. occurs (143), followed by pouring into aq. gives (yields: 97% (141), 06% (142), 90% (143)) 4-chloro-3-nitrobenzoic acid [Beil. IX-402, IX<sub>1</sub>-(165)], cryst. from hot aq., m.p. 184° (142), 182° cor. (141), 180° (143). — [Note that boilg. conc.  $HNO_3$  ( $D = 1.42$ ) has no action (143) on  $\bar{C}$ ; that the crude mononitration prod. sometimes (143) contains a small amt. of *p*-chloronitrobenzene, m.p. 82°; and that the other possible mononitration isomer, viz., 4-chloro-2-nitrobenzoic acid [Beil. IX-401, IX<sub>1</sub>-(165)], m.p. 140°, is not formed in appreciable amt. by direct nitration of  $\bar{C}$ .]

$\bar{C}$  on dinitration, e.g., with 20 wt. pts. conc.  $H_2SO_4$  + 3.3 wt. pts.  $KNO_3$  at 140° for 1½ hrs. (144), or with 12½ wt. pts. conc.  $H_2SO_4$  + 2.4 wt. pts. fuming  $HNO_3$  ( $D = 1.5$ ) at 135–140° for 2 hrs. (145), then poured into aq., gives (yields: 95% (144), 82% (145)) 4-chloro-3,5-dinitrobenzoic acid [Beil. IX-416], pr. from  $C_6H_6$ , m.p. 159° (144) (145). For use in detection of  $\bar{C}$  see (161). — [Note that none of the three other isomeric 4-chloro-dinitrobenzoic acids has ever been reported.]

[ $\bar{C}$  on sulfonation with  $SO_3$  in fuming  $H_2SO_4$  (52) (146) (147) gives 4-chloro-3-sulfo-benzoic acid [Beil. XI-387].]

— Methyl *p*-chlorobenzoate: m.p. 43° (see 3:0535).

— Ethyl *p*-chlorobenzoate: oil, b.p. 238° (see 3:6750).

① *p*-Nitrobenzyl *p*-chlorobenzoate: m.p. 130° (148). [From  $\bar{C}$  (as Na $\bar{A}$ ) with *p*-nitrobenzyl bromide (m.p. 99°) in boilg. alc. (148).]

② Phenacyl *p*-chlorobenzoate: m.p. 89.5° (149), 87.6° (32). [From  $\bar{C}$  as (Na $\bar{A}$ ) with phenacyl bromide (m.p. 50°) in boilg. alc. (98% yield (32)). — Note that the m.p. of this prod. is only slightly higher than that (85.5°) of the corresp. prod. similarly obtd. from *o*-chlorobenzoic acid (3:4150).]

— *p*-Chlorophenacyl *p*-chlorobenzoate: unreported.

③ *p*-Bromophenacyl *p*-chlorobenzoate: m.p. 126° (32). [From  $\bar{C}$  (as Na $\bar{A}$ ) with *p*-bromophenacyl bromide (m.p. 109°) in boilg. alc. (80% yield (32)).]

— *p*-Iodophenacyl *p*-chlorobenzoate: unreported.

④ *p*-Phenylphenacyl *p*-chlorobenzoate: m.p. 160° cor. (150). [From  $\bar{C}$  (as Na $\bar{A}$ ) with *p*-phenylphenacyl bromide (m.p. 126°) in boilg. alc. (150). — Note that m.p. of this prod. is only slightly higher than that (154°) of corresp. prod. similarly obtd. from *m*-chlorobenzoic acid (3:4392).]





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(91) Skrup, Guggenheimer, *Ber.* 53, 114 (1897). (87) Anschütz, Moore, *Ann.* 239, 343-340 (1887). (88) Meyer, *Monatsh.* 30, 730 (1915). (89) M.L.B., *Ger.* 282,134, Feb. 15, 1915; *Cent.* 1915, I 461. (90) Iremescu, Chirnoara, *Z. anal. Chem.* 125, 32-37 (1942); 135 (1943); 12, 12-14 (1932). (82) 31, II 407; *Brit.* 307,223, March 28, 1927; C.A. 22, 2372 (1928).

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# 3:4941 TETRACHLOROHYDROQUINONE


 $C_6H_2Cl_2O_2$ 

Bell VI - 851

VI-(417)

V-(816)

- M.P. 236-237° (1)  
 236° (2)  
 235-236° (3)  
 231° (14)  
 232° (1)  
 230-232° (5)  
 230-231° (6)  
 230° (7) (19)

[See also tetrachlorobenzoquinone-1,4 (chloranil) (3:4978)]

Colorless scales or nids from  $C_6H_6$ , solvated pr. from AcOH losing solvate in air (2) (5). — For crystallographic data see (9). —  $\bar{C}$  sublimates with partial decompn. (10); for study of sublimation pressure see (11).

$\bar{C}$  is insol. aq.; almost insol.  $C_6H_6$ ,  $CCl_4$ ,  $CS_2$ ; exs. sol. alc., ether; spar. sol. AcOH.

[For study of lit. of formn. of  $\bar{C}$  see (12); for studies of heat of combustion see (13) (14)]

[For patent on use of  $\bar{C}$  as vulcanization accelerator see (15).]

## PREPARATION OF $\bar{C}$

From tetrachlorobenzoquinone-1,4. For prepn. of  $\bar{C}$  from chloranil (3:4978) by reduction with various reagents see the following. [For use of aq.  $SO_2$  see (10) (16) (note, however, that this reduction is so slow that it has been used (18) as a method of repn. of 2,3,5-trichlorobenzoquinone-1,4 (3:4672) from tetrachlorobenzoquinone-1,4 (3:4978), and also that during the process substantial amounts of trichlorohydroquinone-sulfonic acid and of dichlorohydroquinone di-sulfonic acid are formed (16)); for use of boilg. conc. HCl (9), conc. HBr (9) (10) in AcOH (3), with conc. III + red (18) or yellow (20) phosphorus, or

with KI or NaI in cold acetone (38) see indic. refs.; for use of  $\text{H}_2\text{S}$  (5),  $\text{SnCl}_2 + \text{HCl}$  (9) (8) (6), aq. slightly alkaline hydroxylamine (13), alc. hydrazine hydrate (21), with EtOH on exposure to direct sunlight (7) (study of quantum efficiency of the photochemical reduction (22)), or with hydroquinone (1:1590) in ether (39) see indic. refs.]

[For formn. of  $\bar{\text{C}}$  as hy-product of use of tetrachlorobenzoquinone-1,4 (chloranil) (3:4978) in low-temp. dehydrogenations see (23) (24); for formn. of derivatives (ethers) of  $\bar{\text{C}}$  as hy-products of reaction of chloranil (3:4978) with free radicals see (25) (26) cf. (27); for formn. of  $\bar{\text{C}}$  as hy-product of reaction of chloranil (3:4978) with  $\text{C}_6\text{H}_5\text{MgBr}$  see (31).]

From 2,3,5-trichlorobenzoquinone-1,4. [For prepn. of  $\bar{\text{C}}$  from 2,3,5-trichlorobenzoquinone-1,4 (3:4672) with conc. HCl on protracted boilg. (9) (28), with fuming HCl in s.t. at  $120^\circ$  for 12 hrs. (29), or in AcOH soln. with dry HCl gas (30) see indic. refs.]

From other sources. [For formn. of  $\bar{\text{C}}$  from hydroquinone (1:1590) in AcOH with  $\text{Cl}_2$  (32), or from *p*-nitroaniline (or certain derivatives) with conc. HCl in s.t. at  $180^\circ$  (2), see indic. refs.]

### CHEMICAL BEHAVIOR OF $\bar{\text{C}}$

Oxidation of  $\bar{\text{C}}$ .  $\bar{\text{C}}$  on oxidation, e.g., with aq. alc.  $\text{AgNO}_3$  (10),  $\text{NH}_4\text{OH}/\text{AgNO}_3$  (2), boilg. conc.  $\text{HNO}_3$  (2) (20), etc., gives tetrachlorobenzoquinone-1,4 (chloranil) (3:4978).

[For studies of oxidn.-reductn. potential of system  $\bar{\text{C}}$  + chloranil see (33) (34) (35) (1) (27) (6).]

[Note also that the quinhydrone to be expected from  $\bar{\text{C}}$  with 1 mole of the corresp. tetrachlorobenzoquinone-1,4 (chloranil) (3:4978) is not reported.]

[Note also that, although  $\bar{\text{C}}$  dissolves in aq. KOH without discoloration, the soln. upon exposure to air turns brown and on stdg. ppts. (16) di-potassium salt of chloranilic acid (2,5-dichloro-3,6-dihydroxybenzoquinone-1,4) (3:4970).]

Other reactions of  $\bar{\text{C}}$ . [ $\bar{\text{C}}$  with  $\text{PCl}_5$  (2 moles) gives (16) hexachlorobenzene (3:4939). —  $\bar{\text{C}}$  with 2,3,5-trichlorobenzoquinone (3:4052) + a little aq. htd. at  $100^\circ$  for  $\frac{1}{2}$  hr. undergoes a redistribution reaction (28) cf. (36).]

- ① Tetrachlorohydroquinone dimethyl ether: m.p.  $164^\circ$  (37),  $160^\circ$  (5). [From  $\bar{\text{C}}$  by action of diazomethane in ether soln. (5).]
- ② Tetrachlorohydroquinone diethyl ether: m.p.  $112^\circ$  (16). [From  $\bar{\text{C}}$  with EtI (2 moles) + KOH (2 moles) in alc. in s.t. at  $130$ – $140^\circ$  (16).]
- ③ Tetrachlorohydroquinone diacetate: m.p.  $245^\circ$  (16),  $244$ – $246^\circ$  (7). [From  $\bar{\text{C}}$  with  $\text{AcCl}$  (3:7065) (16) or from chloranil (3:4978) with  $\text{AcCl}$  in s.t. at  $160$ – $180^\circ$  (16).]
- ④ Tetrachlorohydroquinone dibenzoate: m.p.  $233^\circ$  (9). [From  $\bar{\text{C}}$  with  $\text{BzCl}$  (3:6240) (9).]

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## 3:4942 7-CHLORONAPHTHOIC ACID-1

 $C_{11}H_7O_2Cl$ 

Beil. S.N. 951



M.P. 243° cor. (1)

238-240° (3)

235° (3)

Cryst. from 60% alc. or by sublimation. — Very sol. alc. or AcOH; sol. ether,  $C_6H_6$ . [For prepn. of  $\bar{C}$  from 7-aminonaphthoic acid-1 (1) (2) via diazotization and use of  $Cu_2Cl_2$  reactn. see (1); from 7-chloro-1-(chloromethyl)naphthalene, m.p. 75° (3), by oxdn. with dil.  $HNO_3$  see (3), from 7-chloro-1-bromonaphthalene [Beil. V-548] via conv. to  $RMgBr$  and carbonation see (3).]

$\bar{C}$  with  $PCl_5$  or  $SOCl_2$  yields (1) 7-chloro-1-naphthoyl chloride, yel. cryst. from pet. eth., m.p. 106° cor (1).

① Methyl 7-chloro-1-naphthoate: cryst from 60% MeOH, m.p. 54° cor. (1). [From  $\bar{C}$  in MeOH with conc.  $H_2SO_4$  (90% yield (1)).]

— Ethyl 7-chloro-1-naphthoate: unreported.

② *p*-Bromophenacyl 7-chloro-1-naphthoate: m.p. 145-146° (3).

③ 7-Chloro-1-naphthoamide: colorless ndls. from 50% alc., m.p. 237° cor. (1). [From the acid chloride (above) with 4 pts. conc. aq.  $NH_4OH$  at ord. temp. for 2 hrs. (75% yield (1)).]

④ 7-Chloro-1-naphthoanilide: brownish ndls. from dil. alc., m.p. 185° cor. (1). [From the acid chloride (above) with 5 pts. aniline at 100° (50% yield (1)).]

3:4942 (1) Goldstein, Fischer, *Helv. Chim. Acta* 21, 1519-1521 (1938). (2) Harrison, Royle, *J. Chem. Soc.* 1926, 87. (3) Horn, Warren, *J. Chem. Soc.* 1946, 144.

## 3:4944 5-CHLORONAPHTHOIC ACID-1

 $C_{11}H_7O_2Cl$ 

Beil. IX -651

IX<sub>1</sub>—

M.P. 245° (1)

244-245° (3)

Ndls. which sublime even below m.p. — Eas sol. alc, spar. sol.  $C_6H_6$  or AcOH.

[For prepn. of  $\bar{C}$  from  $\alpha$ -naphthoic acid (1:0785) with  $Cl_2$  in AcOH contg.  $I_2$  (some of the isomeric 8-chloronaphthoic acid-1 (3:4680) also being formed) see (1); from 5-chloro-1-naphthonitrile (see below) on hydrolysis with fuming  $HCl$  in a.t. see (1); from 5-aminonaphthoic acid-1 [Beil. XIV-533] via diazotization and use of  $Cu_2Cl_2$  reactn. see (1); for

formn. (together with other prods.) from  $\alpha$ -naphthoic acid (1:0785) via reactn. with  $\text{Hg}(\text{OAc})_2$  followed by treat. with  $\text{Cl}_2$  in  $\text{AcOH}$  see (3).]

Salts.  $\text{Ca}\bar{\text{A}}_2 \cdot 2\text{H}_2\text{O}$ ; sol. in 116 pts. aq. at ord. temp. (1).

$\bar{\text{C}}$  on soln. in red. fumg.  $\text{HNO}_3$  gives (2) on cooling 5-chloro-8-nitro $\alpha$ naphthoic acid-1 [Beil. IX-654], ndls. from alc., m.p. 224–225° dec. (2) (ethyl ester, m.p. 121° (2)); if the soln. of  $\bar{\text{C}}$  in red fumg.  $\text{HNO}_3$  be heated there is also formed (2) some 4-chloro-1,8-dinitro-naphthalene [Beil. V-561], pale yel. ndls. from  $\text{AcOH}$ , m.p. 180° (3), 175° (2).

— Methyl 5-chloro-1-naphthoate: unreported.

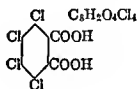
⑦ Ethyl 5-chloro-1-naphthoate: thls. from alc., m.p. 42° (1). [From  $\text{Ag}\bar{\text{A}}$  with  $\text{EtI}$  in s.t. at 100° (1).]

— 5-Chloro-1-naphthonitrile: ndls. from alc., m.p. 145° (1). [From  $\alpha$ -naphthonitrile [Beil. IX-649, IX<sub>1</sub>-(275)] with  $\text{Cl}_2$  in  $\text{CS}_2$  contg.  $\text{I}_2$  (1).]

— 5-Chloro-1-naphthoamide: lfts. or ndls. from warm alc., m.p. 239° (1). [From 5-chloro-1-naphthonitrile (above) on boilg. with alc.  $\text{KOH}$  for several hrs. (1).]

3:4944 (1) Ekstrand, *J. prakt. Chem.* (2) 38, 147–150 (1888). (2) Ref. 1, pp 170–171. (3) Atterburg, *Ber.* 9, 923 (1876). (3) Whitmore, Fox, *J. Am. Chem. Soc.* 51, 3366–3367 (1929).

### 3:4946 TETRACHLOROPHTHALIC ACID



Beil. IX - 819  
IX<sub>1</sub>-(366)

M.P. See text.

[See also tetrachlorophthalic anhydride (3:4947).]

Colorless lfts., thls., or ndls. from aq. invariably contg.  $\frac{1}{2} \text{H}_2\text{O}$ , and therefore giving in this form Neut. Eq. = 156.5. — This hemihydrate can be recrystd. from anhyd. ether without change. — From anhyd. acetone the acid separates in cryst. contg. combined solv. lost in stream of dry air at room temp., yielding anhyd.  $\bar{\text{C}}$ , Neut. Eq. 152, which absorbs aq. from air giving hemihydrate. —  $\bar{\text{C}}$  on htg. at 98° or above, or on attempts to recryst. from dry  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ , or higher-boilg. solvents, or on long dryiog over  $\text{P}_2\text{O}_5$  in vac., is converted to tetrachlorophthalic anhydride (3:4947); for this reason the m.p. observed for  $\bar{\text{C}}$  is always actually that of the corresponding anhydride. — For purification of comml.  $\bar{\text{C}}$  see (1) (13).

$\bar{\text{C}}$  is spar. sol. aq., e.g., 100 g. aq. at 14° dis. 0.57 g., at 99° 3.03 g. of hemihydrate (2);  $\bar{\text{C}}$  is eas. sol. alc. or ether (2); extremely sol. in acetone (1); spar. sol.  $\text{C}_6\text{H}_6$  or  $\text{CHCl}_3$  (2). —  $\bar{\text{C}}$  is sol. in hot aq.  $\text{Na}_2\text{CO}_3$  soln. (dif. from tetrachlorophthalic anhydride (3:4947)).

[For prepn. of  $\bar{\text{C}}$  via hydrolysis of tetrachlorophthalic anhydride (3:4947) see that epd.; other methods include the following: from phthalic anhydride (1:0725) (3), from phthalyl dichloride (3:6900) (4), or phthalic acid (1:0820) (5) with  $\text{Cl}_2$  in pres. of Fe or  $\text{FeCl}_3$  see indie. refs.; from 2-(trichloroacetyl)-3,4,5,6-tetrachlorobenzoic acid [Beil. X-693], with dil. aq.  $\text{NaOH}$  see (6); from 2-(pentachlorobenzoyl)-3,4,5,6-tetrachlorobenzoic acid [Beil. X<sub>1</sub>-353], with conc.  $\text{H}_2\text{SO}_4$  at 200–250° (pentachlorobenzene (3:2290) is also formed) see (7); from naphthoquinone-1,2 (1:9062), anthraquinone (1:9095), 1,2,3,4,5,6,7-heptachloro-anthraquinone [Beil. VII<sub>1</sub>-(414)], or 2-(pentachlorobenzoyl)-3,4,5,6-tetrachlorobenzoic acid (see above) on boilg. with excess  $\text{SbCl}_5$  + a little  $\text{I}_2$  see (7) (8); from 1,2,3,4,5-pentachloronaphthalene [Beil. V-546] (9) (10), 1,2,3,4,5,6,8-heptachloronaphthalene [Beil. V-547] (11), or octachloro $\alpha$ naphthalene (3:4893) (12) by oxidn. with  $\text{HNO}_3$  in s.t. as directed

see indic. refs.; from 2,5,6,7,8-pentachloronaphthoquinone-1,4 [Beil. VII-731] by oxidn. with  $\text{CrO}_3$  or  $\text{HNO}_3$  see (11).]

[ $\bar{\text{C}}$  with  $\text{Na}/\text{Hg}$  in dil. aq. alc. (10) (2) yields phthalic acid (1:0825), but  $\bar{\text{C}}$  in 96% alc. with  $\text{Na}/\text{Hg}$  is practically unaffected (1) (2). —  $\bar{\text{C}}$  with  $\text{H}_2$  in pres. of finely divided  $\text{Ni}$  at  $190^\circ$  and 20 atm. press. yields (14) 4,5,6,7-tetrachlorophthalide [Beil. XVII-312], m.p.  $208.5^\circ$  cor. —  $\bar{\text{C}}$  with  $\text{H}_1 + \text{P}$  in s.t. nt  $230^\circ$  for 6 hrs. yields (2) 4,5,6,7-tetrachlorophthalane [Beil. XVII-51], ndls. from toluene, m.p.  $218^\circ$  (2) (unsol. in boilg. aq.  $\text{NaOH}$ ), accompanied by a little 4,5,6,7-tetrachlorophthalide (above) (sol. in boilg. aq.  $\text{NaOH}$ ).]

$\bar{\text{C}}$  with  $\text{CrO}_3$  oxidizes much more slowly (2) than phthalic acid (1:0825) and is very resistant toward  $\text{HNO}_3$  (2); for detn. of chlorine in  $\bar{\text{C}}$  see (1) (16)

[ $\bar{\text{C}}$  with aq.  $\text{KOH} + \text{KCN} + \text{CuCN}$  htd. under press. at  $180^\circ$  for 8–10 hrs. gives (60% yield (15)) benzenhexacarboxylic acid (mellitic acid) [Beil. IX-1008, IX-1-443]. —  $\bar{\text{C}}$  with  $\text{HBr} + \text{H}_3\text{PO}_4$  in nitrobenzene in pres. of  $\text{CuCl}_2$  yields (17) mixts. of bromotrichlorophthalic acids and dibromodichlorophthalic acids. — For actn. of  $\text{PCl}_5$  see under tetrachlorophthalic anhydride (3:4947). —  $\bar{\text{C}}$  with hydrazine hydrate at  $150^\circ$  gives only (18) *N*-aminotetrachlorophthalimide, colorless ndls. from  $\text{AcOH}$ , m.p.  $288^\circ$  dec. (18); earlier opinions (19) (20) that this prod. was tetrachlorophthalcyclohydrazide have been shown (18) to be erroneous. —  $\bar{\text{C}}$  with steam passed over cat. at  $380\text{--}420^\circ$  loses  $\text{CO}_2$  presumably yielding (21) 2,3,4,5-tetrachlorobenzoic acid [Beil. IX-346], m.p.  $186^\circ$ .]

[For use of  $\bar{\text{C}}$  as softener for animal fibers see (22) (23). — For use of  $\bar{\text{C}}$  in prepn. of  $\alpha$ -borneol (1:5990) from turpentine oil (crude pinene) by htg. at  $108^\circ$  for 12 hrs., removal of unchanged terpenes by distn. and alc.  $\text{NaOH}$  saponification of the remaining di-bornyl tetrachlorophthalate, white cryst. from ether, m.p.  $128\text{--}129^\circ$  (24), see (24) (25).]

Salts.  $\text{K}_2\bar{\text{A}}$ , very sol. aq., spar. sol. alc. (2),  $\text{Ba}_2\bar{\text{A}} \cdot 2\frac{1}{2}\text{H}_2\text{O}$  see (2);  $\text{Ca}\bar{\text{A}}$ , on htg. gives octachloroanthraquinone [Beil. VII-789] (17);  $\text{Cu}_2\bar{\text{A}} \cdot 2\text{H}_2\text{O}$ , spar. sol. aq. (2) (earlier report (27) that on dry distn. it gives dodecachlorofluorane later seriously questioned (28));  $\text{Zn}\bar{\text{A}}$ , very sol. aq. (more sol. cold aq. than hot aq.) (2);  $\text{Ag}_2\bar{\text{A}}$ , spar. sol. aq.

⑧ Dimethyl tetrachlorophthalate: cryst. from  $\text{MeOH}$ , m.p.  $92^\circ$  (2). [From  $\text{Ag}_2\bar{\text{A}}$  with  $\text{MeI}$  (2), from *sym*-tetrachlorophthalyl (di)chloride with  $\text{NaOMe}$  (2) or from  $\bar{\text{C}}$  in 10% aq.  $\text{NaOH}$  (3 moles) on warming with  $\text{Me}_2\text{SO}_4$  (29); note that  $\bar{\text{C}}$  in  $\text{MeOH}$  satd. with  $\text{HCl}$  gas gives (30) only the half ester, methyl hydrogen tetrachlorophthalate, cryst. from  $\text{C}_6\text{H}_6$  on addn. of lgr., m.p.  $142^\circ$  (30) with elimination of  $\text{MeOH}$  and conversion to tetrachlorophthalic anhydride (3:4947) q.v.]

⑨ Diethyl tetrachlorophthalate: cryst., m.p.  $60\text{--}60.5^\circ$  (2) (31). [From  $\text{Ag}_2\bar{\text{A}}$  +  $\text{EtI}$  (2) or from *sym*-tetrachlorophthalyl (di)chloride +  $\text{NaOEt}$  (2); note that *unsym*-tetrachlorophthalyl (di)chloride with abs. alc. nt room temp. gives (31) *pseudo*-diethyl tetrachlorophthalate, thls. from alc., m.p.  $126^\circ$  (19), and that this epd. on stdg. in the reactn. mixt. is partially conv. to the normal ester of m.p.  $60.5^\circ$  (31).]

⑩ Di-(*p*-nitrobenzyl) tetrachlorophthalate: ndls. from  $\text{C}_6\text{H}_6$ , or from aq. alc., m.p.  $180\text{--}181^\circ$  (32),  $179\text{--}180^\circ$  (33) [From  $\text{N}_2\bar{\text{A}}$  + *p*-nitrobenzyl bromide on refluxing in alc. (32), or from  $\text{Ag}_2\bar{\text{A}}$  + *p*-nitrobenzyl iodide (33).]

⑪ Di-(*p*-phenylphenacyl) tetrachlorophthalate: cryst. from acetone, m.p.  $193^\circ$  (34). [From  $\text{Na}_2\bar{\text{A}}$  with *p*-phenylphenacyl bromide (2 moles) on htg. in alc. (34).]

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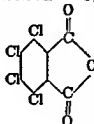
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### 3:4947 TETRACHLOROPHTHALIC ANHYDRIDE

 $C_2O_2Cl_4$ 

Beil. XVII - 484

 XVII<sub>1</sub>-(254)


M.P. 255-257° cor. (1)

255-256.5° cor. (2)

255° (3)

252° (4), cor. (5)

215° u.c. (5)

[See also tetrachlorophthalic acid (3:4946).]

Colorless pr. or ndls. by sublimation. — Insol. cold aq., hut sol. in boilg. aq. because of hydrolysis to tetrachlorophthalic acid (3:4946); spar. sol. ether. —  $\bar{C}$  is insol. in  $Na_2CO_3$  soln. (dif. from tetrachlorophthalic acid (3:4946)).

[For prepn. of  $\bar{C}$  from tetrachlorophthalic acid (3:4946) by htg. above m.p. (6), by htg. 8 hrs. at 110° (7), by htg. 120 hrs. at 100° (8) (9), by sublimation, htg. at 98°, by crystn. from hot  $C_6H_6$ ,  $CHCl_3$ ,  $AcOH$  (2), or by protracted drying over  $P_2O_5$  in vac. (1) cf. (5) (10) see indic. refs.; from phthalic anhydride (1:0725) with  $Cl_2$  in pres. of Fe salts at 160-260° (11), or with  $Cl_2$  in pres. of  $SbCl_5$  at 200° (10) (12), or with  $Cl_2$  in pres. of fung.  $H_2SO_4$  (50-60%  $SO_3$ ) and  $I_2$  (2) (13) see indic. refs.; from naphthalene (1:7200) with  $ClSO_3H$  in s.t. at 180° see (3).]

[ $\bar{C}$  on reduction with Zn dust + hot  $AcOH$  (10) or with  $H_2$  + Ni at 190° and 20 atm. yields (14) 4,5,6,7-tetrachlorophthalide [Beil. XVII-312], m.p. 203.5° cor.]

$\bar{C}$  reacts with monohydric alcs. to yield corresp. half esters: e.g.,  $\bar{C}$  dislvd. in excess warm  $MeOH$ , htd. 5-10 min., evapd. yields (15) methyl hydrogen tetrachlorophthalate [Beil. IX-820], cryst. from hot  $C_6H_6$  on addn. of lgr., m.p. 139-140° (15), 142° (16), Neut. Eq. 318;  $\bar{C}$  with abs.  $EtOH$  treated as for preceding case gives (15) ethyl hydrogen tetrachlorophthalate, m.p. 93-94° (15), 94-95° (10), Neut. Eq. 332. — [ $\bar{C}$  with *ter*-butyloxymagnesium

bromide in ether + dioxane at 50-55° for 1 hr. gives (54% yield (17)) *ter*-butyl hydrogen tetrachlorophthalate, decomposing at 142°, Neut. Eq. 360; for analogous formn. of *ter*-amyl, triethylcarbiny, tri-*n*-propylcarbiny, tri-*n*-butylcarbiny and tri-*n*-amylcarbiny hydrogen tetrachlorophthalates see (17).] — [For reactn. of  $\bar{C}$  with glycerol and use in prepn. of resins of glyptal type see (3) (18).]

$\bar{C}$  with 1 mole  $PCl_5$  in s.t. 4 hrs. at 220° (19) cf. (10) or  $\bar{C}$  with 1 mole  $PCl_5$  +  $POCl_3$  refluxed 72 hrs. (20) gives (90% yield (20)) *unsym.*-tetrachlorophthalyl (di)chloride (3,3,4,5,6,7-hexachlorophthalide) [Beil. XVII-(484)], cryst. from  $C_6H_6$  with 1 mole solvent, m.p. 118° (10) (20), 118-120° (19), but losing  $C_6H_6$  in air to give solvent free cpd., ndls. from pet. ether, m.p. 137° (19) (20); this prod. on distn. (19) undergoes partial rearr. to *sym.*-tetrachlorophthalyl (di)chloride, pr. from pet. ether, m.p. 48° (19). — Note that the latter *sym.*-phthalyl (di)chloride (which is very soluble in most org. solvents) gradually changes even in solid form and very rapidly in solution (particularly in pres. of animal charcoal) to the *unsym.*-tetrachlorophthalyl (di)chloride (which is spar. sol. in most org. solvents) (19). —  $\bar{C}$  with  $SOCl_2$  +  $ZnCl_2$  at 200-240° yields (21) cf. (22) tetrachlorophthalyl (di)chloride but whether the *unsym.* or *sym.* forms or their mixture is not stated. — Note also that with abs. EtOH the *unsym.* acid chloride yields (19) *pseudo* diethyl tetrachlorophthalate, thls. from alc., m.p. 126° (19), while the *sym.* acid chloride gives (19) *sym.* diethyl tetrachlorophthalate, m.p. 60.5° (19).]

$\bar{C}$  with 2 moles  $PCl_5$  in s.t. at 200° for 5-6 hrs. yields (10) a prod. (regarded as either 1,1,3,3,4,5,6,7-octachlorophthalide or 2-(trichloromethyl)-3,4,5,6-tetrachlorobenzoyl chloride), cryst. from ether, m.p. 140° (10), and practically unaffected by warm alc. KOH.]

$\bar{C}$  with arom. hydrocarbons +  $AlCl_3$  yields corresp. *o*-aroyl-tetrachlorobenzoic acids: e.g.,  $\bar{C}$  with  $C_6H_6$  +  $AlCl_3$  (23) (24) (25) or  $\bar{C}$  with  $C_6H_5MgBr$  (26) gives 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid [Beil. X-750], ndls. from 80% AcOH or  $C_6H_6$ , m.p. 201° (24), 200° (23), 188-189° (26), which on ring closure with 20 pts. conc.  $H_2SO_4$  at 200° for 5 min. (23) gives 1,2,3,4-tetrachloroanthraquinone [Beil. VII-789], gold-yel. fls., m.p. 191° (23). —  $\bar{C}$  with toluene +  $AlCl_3$  gives (yields: 100% (27), 95% (23), 94% (29)) 2-(*p*-toluyl)-3,4,5,6-tetrachlorobenzoic acid, cryst. from  $C_6H_6$ , m.p. 174.5° cor. (29), 172° (28) (30) (the value of 142° (27) may be a misprint for 172°), which on ring closure with 12 pts.  $H_2SO_4 \cdot H_2O$  at 190-200° for 2 min. (27) or with 9 pts. fuming  $H_2SO_4$  (2%  $SO_3$ ) at 120-130° for 30 min. (28) gives (21% yield (28)) 2-methyl-5,6,7,8-tetrachloroanthraquinone, yel. ndls. from toluene, m.p. 195-196° (27), or from EtOAc, m.p. 102° (28). — For corresp. reactns. of  $\bar{C}$  with *o*-xylene (1:7430), *m*-xylene (1:7430), *p*-xylene (1:7415), and ethylbenzene (1:7410) and use in identif. of these cpds. see (7). — For reactn. of  $\bar{C}$  with  $\alpha$ -naphthyl  $MgBr$ , *p*-methoxyphenyl  $MgBr$ , or *p*-bromophenyl  $MgBr$  yielding corresp. *o*-aroyl-tetrachlorobenzoic acids see (26).]

$\bar{C}$  with chlorobenzene (3:7903) +  $AlCl_3$  at 140° for 3 hrs. gives (92% yield (31)) 2-(*p*-chlorobenzoyl)-3,4,5,6-tetrachlorobenzoic acid, cryst. from AcOH, m.p. 162-165° (31), which with conc.  $H_2SO_4$  at 140° for 30 min. gives 2,5,6,7,8-pentachloroanthraquinone, yel. cryst. from AcOH, m.p. 192° (31). — For corresp. reactns. of  $\bar{C}$  with *p*-dichlorobenzene (3:9950), with 1,2,4-trichlorobenzene (3:6120), or with nitrobenzene see (31).]

$\bar{C}$  with phenols and appropriate condensing agents gives two different types of reactns. according to circumstances, viz., formation of corresp. *o*-hydroxyaroyl-tetrachlorobenzoic acids (cf. above) or of corresp. tetrachlorophthalic acids. — E.g.,  $\bar{C}$  with 1 mole phenol +  $AlCl_3$  in acetylene tetrachloride at 125° for 3 hrs. gives (yields: 79% (32), 82% (33)) 2-(*o*-hydroxybenzoyl)-3,4,5,6-tetrachlorobenzoic acid [Beil. XI-(470)], fls. from xylene/AcOH, m.p. 216-218° cor. (32), 210° (33), which with boilg. NaOH loses HCl and ring-closes to 2,3,4-trichloroxanthonecarboxylic acid-2 [Beil. XVIII-(499)], colorless ndls. from alc., m.p. 261-264° cor. (32), 262-265° dec. (33). — For corresp. reactns. of  $\bar{C}$  with



*o*-cresol (1:1400) (32) (34), *m*-cresol (1:1730) (32), *p*-cresol (1:1410) (32),  $\alpha$ -naphthol (1:1500) (38),  $\beta$ -naphthol (1:1540) (32), *nn*-isole (1:7445) (34) see indie. refs., with hydroquinone (1:1590) +  $\text{AlCl}_3$  +  $\text{NaCl}$  at 150–155° for 1½ hrs. giving 82% yield 2-(2',5'-dihydroxybenzoyl)-3,4,5,6-tetrachlorobenzoic acid, m.p. 231°, or on further htg. in the above melt at 210–215° for 1 hr. ring closing to 1,4-dihydroxy-5,6,7,8-tetrachloroanthraquinone, red cryst. from xylene, m.p. 247°, see (35). — However,  $\bar{\text{C}}$  with 2 moles phenol in pres. of fuming  $\text{H}_2\text{SO}_4$  (20%  $\text{SO}_3$ ) as directed (8) (36) gives 65% yield phenoltetrachlorophthalcin [Beil. XVIII-148, XVIII-1-(375)], m.p. 316–317° dec. (36), accompanied by about 10% (37) of 3',4',5',6'-tetrachlorofluoran [Beil. XIX-148, XIX-1-(076)], colorless pr. from  $\text{C}_6\text{H}_6$ , m.p. 298° dec. (33), 290–291° (37) (for sepn. of this by-prod. from the phenoltetrachlorophthalcin see (37)). — For condens. of  $\bar{\text{C}}$  with *o*-cresol (1:1400) to *o*-cresoltetrachlorophthalcin see (45); with resorcinol (1:1539) to 3',4',5',6'-tetrachlorofluorescein [Beil. XIX-227, XIX-1-(722)] see (10) (9).]

[For condens. of  $\bar{\text{C}}$  with *m*-diethylaminophenol see (39); with *N*-aryl-*m*-aminophenols in prepn. of phthalcin dyes see (40); for condens. of  $\bar{\text{C}}$  with hydroxyisodibenzanthrone in prepn. of vat dyes see (41); for use of  $\bar{\text{C}}$  as textile softener see (42).]

[ $\bar{\text{C}}$  with steam passed over cat. at 380–420° loses  $\text{CO}_2$  presumably yielding (43) 2,3,4,5-tetrachlorobenzoic acid [Beil. IX-346], m.p. 186°.]

$\bar{\text{C}}$  on fusion and treatment with  $\text{NH}_3$  gas (10) (4), or on warming with formamide (2), or on fusion with  $(\text{NH}_4)_2\text{CO}_3$  (47) gives (yields: 91% (2), 90% (47)) tetrachlorophthalimide [Beil. XXI-505, XXI-1-(391)], lfts. from  $\text{AcOH}$ , dimethylaniline or nitrobenzene, m.p. 338–339° cor. (2), 336–337° (47); for reactn. of this prod. with  $\text{KOMe}$  forming *K* tetrachlorophthalimide and use of latter in identification of alkyl halides, etc., see (47). — [For reactn. of  $\bar{\text{C}}$  with hydrazine hydrate in dil. alc. yielding *N*-aminotetrachlorophthalimide, ndls. from  $\text{AcOH}$ , m.p. 288° dec., see (48); for reactn. of  $\bar{\text{C}}$  with hydroxylamine in aq. and in  $\text{MeOH}$  see (49). —  $\bar{\text{C}}$  in boilg.  $\text{AcOH}$  treated with *nn*-line yields (2) cf. (50) *N*-phenyl-tetrachlorophthalimide (tetrachlorophthalanil) [Beil. XXI-505, XXI-1-(391)], m.p. 274–275° cor. (2). — For reactn. of  $\bar{\text{C}}$  with  $\alpha$ -phenylenediamine see (6).]

$\bar{\text{C}}$  on warming with aq., or with nq. alk. followed by acidification, yields tetrachlorophthalic acid (3:4910) q.v. [For use of differential hydrolysis of  $\bar{\text{C}}$  in sepn. from 3,4-dichlorophthalic anhydride (3:3095), 3,6-dichlorophthalic anhydride (3:4860), or 4,5-dichlorophthalic anhydride (3:4830) see under these epds.]

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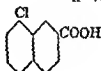
1921, IV 127; Swiss 89,039, Aug. 1, 1921; *Cent.* 1922, II 145; Ger. 360,422, Oct. 2, 1922; *Cent.* 1923, II 190.

(31) Hofmann, *Monatsh.* 36, 812-818 (1915). (32) Ullmann, Schmidt, *Ber.* 52, 2113-2118 (1919). (33) Ullmann, Schmidt, *Ber.* 48, 283-285 (1925). (34) Orndorff, Murray, *J. Am. Chem. Soc.* 19, 111-112 (1897). (35) Ullmann, *J. prakt. Chem.* (2) 147, 333 (1930/1937). (36) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (37) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (38) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (39) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (40) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (41) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (42) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (43) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (44) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (45) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (46) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (47) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (48) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (49) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (50) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (51) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (52) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (53) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (54) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (55) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (56) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (57) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (58) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (59) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (60) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (61) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (62) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (63) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (64) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (65) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (66) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (67) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (68) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (69) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (70) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (71) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (72) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (73) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (74) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (75) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (76) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (77) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (78) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (79) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (80) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (81) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (82) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (83) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (84) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (85) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (86) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (87) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (88) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (89) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (90) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (91) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (92) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (93) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (94) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (95) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (96) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (97) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (98) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (99) Orndorff, Kennedy, *ibid.* 33, 2487 (1910). (100) Orndorff, Kennedy, *ibid.* 33, 2487 (1910).

### 3:4948 8-CHLORONAPHTHOIC ACID-2

 $C_{10}H_7O_2Cl$ 

Beil. IX - 662

 IX<sub>1</sub>—


M.P. 260° (1)

Fine ndls. best purified by sublimation (1)

[For prepn. of  $\bar{C}$  from 8-aminonaphthoic acid-2 [Beil. XIV-536] via diazotization and use of  $Cu_2Cl_2$  reactn. see (1).]

Salts. (1).  $Ca\bar{A}_2 \cdot 7H_2O$ ;  $Ba\bar{A}_2 \cdot 6H_2O$ ; both spar. sol. cold aq. but eas. sol. hot aq.

$\bar{C}$  with  $Cl_2$  in AcOH contg.  $I_2$  yields (1) 5,8-dichloronaphthoic acid-2 [Beil. IX-662], mulls. from alc., m.p. 237° (1) (ethyl ester, m.p. 64-65° (1)).

— Methyl 8-chloro-2-naphthoate: unreported.

Ⓔ Ethyl 8-chloro-2-naphthoate: lfts. from alc., m.p. about 29° (1). [From  $\bar{C}$  in EtOH with dry HCl gas (1).]

3:4948 (1) Ekstrand, *J. prakt. Chem.* (2) 43, 417-418, 421 (1891).

### 3:4950 3,5-DICHLORO-4-HYDROXYBENZOIC ACID

 $C_7H_4O_3Cl_2$ 

Beil. X - 176

 X<sub>1</sub>-( 78)


M.P. 268-269° cor. (1)

265° cor. (2)

265° (3)

259-260° (4)

257-258.5° (5)

255-256° (6) (9)

White ndls. from dil. alc. or dil. AcOH; spar. sol. cold but more sol. hot aq; eas. sol. alc., ether; sublimes at 250-260° (7) without appreciable decompn. (6).

[For prepn. of  $\bar{C}$  from *p*-hydroxybenzoic acid (1:0840) in 10% AcOH (1) or in aq. KOH (3 moles) (7) with  $Cl_2$ , or on htg. with  $SbCl_5$  (4 moles) (6) or with 30%  $H_2O_2$  + HCl as directed (80% yield (8)) see indic. refs.; from 3-sulfo-4-hydroxybenzoic acid in aq. with

Cl<sub>2</sub> see (9); from potassium 2,6-dichlorophenolate with CO<sub>2</sub> at 140° see (7); from ethyl 3,5-dichloro-4-hydroxybenzoate (see below) by hydrolysis with 35% aq. KOH (5) or with Claisen's alk. (95% yield (1)) see indic. refs.; from 3,5-dichloro-4-methoxybenzoic acid with 45% HI for 15 hrs. in s.t. at 130-140° see (3) (2).]

$\bar{C}$  on bfg with CaO (4) (7), or with dimethylaniline at 190° (78% yield (1)), or with quinoline at 190-200° (80-85% yield (10)) loses CO<sub>2</sub> giving 2,6-dichlorophenol (3:1595).

$\bar{C}$  in conc. aq. soln. gives with FeCl<sub>3</sub> a brown ppt. (4).

[ $\bar{C}$  on electrolytic reduction in aq./alc./H<sub>2</sub>SO<sub>4</sub> gives (11) 3,5-dichloro-4-hydroxybenzyl ethyl ether [Beil. VI-898], m.p. 86° (11); for prepn. and study of thermal rearr. of the crotyl ether of  $\bar{C}$  see (1).]

① Methyl 3,5-dichloro-4-hydroxybenzoate: ndls. from dil. alc. or lgr., m.p. 124° (3), 122° (12), 121-122° (4) (5). [From  $\bar{C}$  in MeOH by satn. with HCl gas (3) (4); also from methyl *p*-hydroxybenzoate (1:1549) with SO<sub>2</sub>Cl<sub>2</sub> (2 moles) (5).] [This prod. with acetyl chloride yields (5) corresp. acetate, lfts. from MeOH, m.p. 70-71° (5), 68-69° (4).]

② Ethyl 3,5-dichloro-4-hydroxybenzoate: ndls. of monohydrate, m.p. 108-116° cor. (1), 116° (5) from 80% alc.; after long drying in vac. over P<sub>2</sub>O<sub>5</sub> lose aq. yielding anhydrous ester, m.p. 111-112° cor. (1); note that this ester is extracted from ether soln. by aq. NaHCO<sub>3</sub> and is also titratable with stand. alk. (Neut. Eq. of monohydrate 253). [From ethyl *p*-hydroxybenzoate (1:1534) with excess SO<sub>2</sub>Cl<sub>2</sub> (5) in 85% yield (1).]

3:4950 (1) Tarbell, Wilson, *J. Am. Chem. Soc.* 64, 1066-1070 (1942). (2) Durrans, *J. Chem. Soc.* 123, 1426 (1923). (3) Bertozzi, *Gazz. chim. ital.* 29, 11 39 (1899). (4) Zincke, *Ann.* 261, 250-252 (1891). (5) Mazzara, *Gazz. chim. ital.* 29, I 387-388 (1899). (6) Lössner, *J. prakt. Chem.* (2) 13, 434 (1876). (7) Tarugi, *Gazz. chim. ital.* 30, 11 490-491 (1900). (8) Leulier, *Pinet. Bull. soc. chim.* (4) 41, 1365-1366 (1927). (9) Datta, *Mitter, J. Am. Chem. Soc.* 41, 2038 (1919) (10) Blicke, Smith, Powers, *J. Am. Chem. Soc.* 54, 1468 (1932).

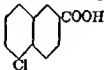
(11) Mettler, *Ber.* 39, 2940 (1906). (12) von Auwers, *Reis, Ber.* 29, 2359 (1896).

### 3:4952 5-CHLORONAPHTHOIC ACID-2

C<sub>11</sub>H<sub>7</sub>O<sub>2</sub>Cl

Beil IX - 662

IX<sub>1</sub>-



M.P. 270° cor. (1)

263° (2)

Ndls. from alc. or AcOH. — Sol. in hot alc., in C<sub>6</sub>H<sub>6</sub> or AcOH. — Sublimes in ndls. even below m.p.

[For prepn. of  $\bar{C}$  from 5-amino-2-naphthoic acid [Beil. XIV-536] via diazotization and use of Cu<sub>2</sub>Cl<sub>2</sub> reactn. see (2); from 5-chloro-2-naphthonitrile (below) by hydrolysis in AcOH/H<sub>2</sub>SO<sub>4</sub>/aq. medium (alm. 100% yield (1)) or with alc. KOH (2) see indic. refs.]

$\bar{C}$  with PCl<sub>5</sub> yields (1) 5-chloro-2-naphthoyl chloride, m.p. 89° cor., sol. in pet. eth. or C<sub>6</sub>H<sub>6</sub>, but only very slowly hydrolyzed by aq. even on hfg. (1).

$\bar{C}$  on mononitration by soln. in excess conc. HNO<sub>3</sub> (*D* = 1.42) yields (2) on cooling 5-chloro-*z*-nitronaphthoic acid-2, ndls. from AcOH, m.p. 271° (ethyl ester, m.p. 118°);  $\bar{C}$  on dinitration with red fumg. HNO<sub>3</sub> + a little conc. H<sub>2</sub>SO<sub>4</sub> yields (1) 5-chloro-*z,y*-dinitronaphthoic acid-2, ndls. from AcOH, m.p. about 243° (ethyl ester, m.p. 132°);  $\bar{C}$  on trinitration by conversion to mononitro- $\bar{C}$  (above) and treatment with excess fumg. HNO<sub>3</sub> + conc. H<sub>2</sub>SO<sub>4</sub> yields (1) 5-chloro-*z,y,z*-trinitronaphthoic acid-2, yel. cryst. from AcOH, m.p. 260-261° dec. (ethyl ester, m.p. 183°).

Salts (2)  $\text{Na}\ddot{\text{A}}\cdot 2\text{H}_2\text{O}$  sol. aq.;  $\text{Ca}\ddot{\text{A}}_2\cdot 3\frac{1}{2}\text{H}_2\text{O}$ , sol. in 4430 pts. cold aq.;  $\text{Ba}\ddot{\text{A}}_2\cdot 4\frac{1}{2}\text{H}_2\text{O}$ , very spar. sol. cold aq.

⑤ Methyl 5-chloro-2-naphthoate: m.p.  $81^\circ$  cor. (1). [From  $\ddot{\text{C}}$  in MeOH with conc.  $\text{H}_2\text{SO}_4$  (90% yield (1)).]


⑥ Ethyl 5-chloro-2-naphthoate: ndls. from alc., m.p.  $45^\circ$  (2).

— 5-Chloro-2-naphthonitrile: ndls. from alc., m.p.  $142^\circ$  cor. (1),  $144^\circ$  (2). [From 2-naphthonitrile (Beil IX-659, IX<sub>1</sub>-(277)) with  $\text{Cl}_2$  in AcOH contg.  $\text{I}_2$  (2) or from 5-amino-2-naphthonitrile (Beil. XIV-536) via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reactn. (28% yield (1)).]

— 5-Chloro-2-naphthoamide: ndls., m.p.  $190.5^\circ$  cor. (1),  $186-187^\circ$  (2). [From 5-chloro-2-naphthentriole (above) by hydrol. with alc. KOH (1) (2) or from acid chloride (above) with 4 pts. conc. aq.  $\text{NH}_4\text{OH}$  for 2 hrs. at ord. temp. (80% yield (1)).]

⑦ 5-Chloro-2-naphthoanilide: m.p.  $202.5^\circ$  cor. (1). [From the acid chloride (above) with 3 pts. aniline at  $100^\circ$  (90% yield (1))]

3:4952 (1) Goldstein, Matthey, *Helv. Chim. Acta* 21, 65-66 (1938). (2) Ekstrand, *J. prakt. Chem.* (2) 43, 411-417 (1891).

3:4960 5-CHLOROISOPHTHALIC ACID   $\text{C}_6\text{H}_4\text{O}_4\text{Cl}$  Beil. IX - 838  
(5-Chlorobenzenedicarboxylic acid-1,3) IX<sub>1</sub>—

M.P.  $278^\circ$  (1)

$\ddot{\text{C}}$  cryst. from aq. in ndls. which even after drying over conc.  $\text{H}_2\text{SO}_4$  cont.  $\frac{1}{2}$  mole  $\text{H}_2\text{O}$ ; this water is lost, however, on htg. at  $120^\circ$  (1). —  $\ddot{\text{C}}$  is sol. at  $15^\circ$  in 3450 pts. aq. (1).


[For prepn. of  $\ddot{\text{C}}$  from 5-aminobenzenedicarboxylic acid-1,3 (5-aminoisophthalic acid) (Beil XIV-556, XIV<sub>1</sub>-(636)) via diazotization and htg. sepg. diazonium salt with strong HCl see (1); from 5-chloro-3-methylbenzoic acid (3.4715) by oxdn. with  $\text{KMnO}_4$  in dil. aq. KOH see (2).]

Salts.  $\text{Na}\ddot{\text{A}}$ ,  $\text{K}\ddot{\text{A}}$ , eas. sol. aq. or alc.;  $\text{Ag}\ddot{\text{A}}$ , ndls. from aq.;  $\text{Mg}\ddot{\text{A}}$ ,  $7\text{H}_2\text{O}$ ;  $\text{Ca}\ddot{\text{A}}$ ,  $2\text{H}_2\text{O}$ , sol. at  $15^\circ$  in 28 pts. aq.;  $\text{Sr}\ddot{\text{A}}$ ,  $\text{H}_2\text{O}$ , sol. at  $15^\circ$  in 108 pts. aq.;  $\text{Ba}\ddot{\text{A}}$ ,  $2\text{H}_2\text{O}$  sol. at  $15^\circ$  in 71 pts. aq.;  $\text{Cd}\ddot{\text{A}}$ , sol. at  $15^\circ$  in 330 pts. aq. (for details see (1)).

— Dimethyl 5-chloroisophthalate: unrecorded.

⑧ Diethyl 5-chloroisophthalate: pr. from alc., m.p.  $45^\circ$  (1). [From  $\ddot{\text{C}}$  in EtOH with HCl gas (1).]

3:4960 (1) Beyer, *J. prakt. Chem.* (2) 25, 506-515 (1882) (2) Klages, Knoevenagel, *Ber.* 23, 2045-2046 (1895).

3:4965 4,6-DICHLOROISOPHTHALIC ACID   $\text{C}_6\text{H}_2\text{O}_4\text{Cl}_2$  Beil. IX - 838  
(4,6-Dichlorobenzenedicarboxylic acid-1,3) IX<sub>1</sub>—

M.P.  $279-281^\circ$  (1)

$280^\circ$  u.c. (2)

Colorless ndls. from hot aq. or dil. alc.; eas. sol. alc., ether,  $\text{CHCl}_3$ ; insol. cold aq.

[For prepn. of  $\ddot{\text{C}}$  from 4,6-dichloro-1,3-dimethylbenzene (Beil. V-373, V<sub>2</sub>-(291)) by

oxidn. with 20 pts.  $\text{HNO}_3$  ( $D = 1.18$ ) in s.t. at  $220^\circ$  for several hrs. (2) or with  $\text{CrO}_3/\text{AcOH}$  (2) see indic. refs.; from 1,3-dimethylbenzene-4,6-bis-(sulfonyl chloride) (1) with  $\text{SOCl}_2$  in s.t. at  $240^\circ$  for 36 hrs. see (1).]

$\text{Ag}_2\bar{\text{A}}$ , white ppt. (2),  $\text{Ba}\bar{\text{A}}$ ,  $\text{H}_2\text{O}$  spar. sol. cold aq. but eas. sol. hot aq. (2).

⑥ Dimethyl 4,6-dichloroisophthalate: cryst. from dil. MeOH, m.p.  $97-98^\circ$  (1). [From  $\bar{\text{C}}$  in MeOH on htg. (1).]

⑦ 4,6-Dichloroisophthaldianilide: m.p.  $205^\circ$  (1). [From  $\bar{\text{C}}$  on htg. with aniline (1).]

3:4965 (1) Pollak, Rudich, *Monatsh.* **43**, 221 (1922). (2) Claus, Burstert, *J. prakt. Chem.* (2) **41**, 558-560 (1890).

3:4970 2,5-DICHLORO-3,6-DIHYDROXY-  
BENZOQUINONE-1,4  
(Chloranilic acid)

$\text{C}_6\text{H}_2\text{O}_4\text{Cl}_2$

Beil. VIII - 379  
VIII<sub>1</sub>-



M.P.  $283-284^\circ$  s.t. (1)

$282-284^\circ$  s.t. (2)

Lustrous red lfts. with  $2\text{H}_2\text{O}$  (3) (4) (lost at  $100^\circ$  or slowly on stdg. over conc.  $\text{H}_2\text{SO}_4$  (3) (4)). —  $\bar{\text{C}}$  on slow heating (even in s.t.) sublims without melting; in s.t. inserted in bath or block preheated to about  $278^\circ$ , however, melts as stated above (1).

[For prepn. of  $\bar{\text{C}}$  from chloranil (tetrachlorobenzoquinone-1,4) (3:4978) by actn. of dil. NaOH at  $70-80^\circ$  see (3) (2); for other methods see Beil. VIII-379.]

$\bar{\text{C}}$  is sol. in aq. yielding violet-red solns.; at 13.5 g. 100 pts. aq. dis. 0.19 pt., at  $99^\circ$  1.4 pt. anhyd.  $\bar{\text{C}}$  (3); addn. of HCl or  $\text{H}_2\text{SO}_4$  ppts.  $\bar{\text{C}}$  decolorizing soln. (5).

$\bar{\text{C}}$  behaves as strong dihasic ac. forming stable Na, K, Ba, Ag salts. —  $\text{Na}_2\bar{\text{A}} \cdot 4\text{H}_2\text{O}$ , dark red (7) triclinic (8) pr. sepg. on rapid cooling of warm soln. to  $18^\circ$  (6); loses  $2\text{H}_2\text{O}$  over  $\text{H}_2\text{SO}_4$  and becomes anhyd. at  $110^\circ$  (7). —  $\text{Na}_2\bar{\text{A}} \cdot 3\text{H}_2\text{O}$ , black cryst. sepg. from soln. above  $35^\circ$  (6). —  $\text{Na}_2\bar{\text{A}}$ ; 100 pts. aq. at  $21^\circ$  dis. 1.06 g., at  $99^\circ$  6.19 g. (3). —  $\text{Ag}_2\bar{\text{A}}$ , red ppt. spar. sol. aq. (8a).

$\bar{\text{C}}$  htd. in s.t. with conc.  $\text{H}_2\text{SO}_4$  soln. for some hrs. (9) or treated with Sn + HCl (9) or Na/Hg (9) yields 3,6-dichloro-1,2,4,5-tetrahydroxybenzene (hydrochloranilic acid) [Beil. VI-1156], colorless cryst., no m.p. recorded hut with AcCl in s.t. at  $100^\circ$  yielding tetraacetyl deriv., colorless ndls. from alc. or hy subl., m.p.  $235^\circ$  (9). [Use of insufficient  $\text{SO}_2$  for reduction of  $\bar{\text{C}}$  leads to pptn. of corresp. quinhydrone, fine black ndls. (9).] [For studies of oxidn.-reductn. potential of  $\bar{\text{C}}$  see (2) (10) (11).]

$\bar{\text{C}}$  with alk. +  $\text{I}_2$  — KI soln. yields (12) iodoform, m.p.  $119^\circ$ .

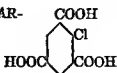
⑧ 2,5-Dichloro-3,6-dimethoxybenzoquinone-1,4 (dimethyl chloranilate) [Beil. VIII-380]: from  $\text{Ag}_2\bar{\text{A}} + \text{CH}_3\text{I}$  (13) or from anhydrous  $\text{K}_2\bar{\text{A}} + \text{Me}_2\text{SO}_4$  (14); red pr. from  $\text{C}_6\text{H}_8$  or  $\text{CHCl}_3$ , m.p.  $141-142^\circ$  (13) (14).

⑨ 2,5-Dichloro-3,6-diacetoxybenzoquinone-1,4 (chloranilic acid diacetate) [Beil. VIII-381]: from finely pdrd.  $\text{Ag}_2\bar{\text{A}} + \text{AcCl}$  in dry ether (15); yel. ndls., m.p.  $182.5^\circ$  (15).

3:4970 (1) Michael, *Ber.* **28**, 1631 (1895) (2) Conant, Fieser, *J. Am. Chem. Soc.* **46**, 1866-1867 (1924). (3) Graebe, *Ann.* **263**, 24-27 (1891). (4) Jackson, MacLaurin, *Am. Chem. J.* **37**, 98-100 (1907). (5) Erdmann, *J. prakt. Chem.* (1) **22**, 285 (1841). (6) Valeur, *Ann. chim.* (7) **21**, 510-512 (1900). (7) Hesse, *Ann.* **114**, 304 (1860). (8) Pope, *J. Chem. Soc.* **61**, 583-584 (1892). (8a) Erdmann, *Ann.* **48**, 317 (1843). (9) Graebe, *Ann.* **146**, 32-36 (1868). (10) Conant, Lutz, *J. Am. Chem. Soc.* **46**, 1257 (1924).

{11} Schwarzenbach, Suter, *Helv. Chim. Acta* **24**, 626-628 (1941). {12} Jackson, Torrey, *Am. Chem. J.* **20**, 429-430 (1898). {13} Kehrman, *J. prakt. Chem.* (2) **40**, 370 (1888), **43**, 260 (1891). {14} Graebe, *Ann.* **340**, 248-249 (1905). {15} Nef, *Am. Chem. J.* **12**, 471-472 (1890); *J. prakt. Chem.* (2) **42**, 169-171 (1890).

**3:4975 2-CHLOROBENZENETRICARBOXYLIC ACID-1,3,5**  
(Chlorotrimelic acid)



$C_9H_5O_6Cl$

Beil. IX - 980  
IX<sub>1</sub>—

M.P. 285° (1) (anhydrous)  
278° (2) (hydrate)

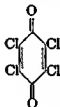
Ndls. or thls. with 1 H<sub>2</sub>O from aq. (2); very readily sol. cold aq. (1) (contrast (2)), extremely eas. sol. hot aq. (1) (2); eas. sol. alc., ether (2); insol. CHCl<sub>3</sub> (2). — Sublimes largely undecomposed (2).

[For prepn. of  $\bar{C}$  from chloromesitylene (3:8725) by oxidn. with aq. KMnO<sub>4</sub> either with or without MgSO<sub>4</sub> (63.5% yield) see (1); from 2-hydroxybenzenetricarboxylic acid-1,3,5 (hydroxytrimelic acid) [Beil. X-580] with PCl<sub>5</sub> (4 moles) followed by hydrolysis (with warm aq. or aq. alk.) of the intermediate *tris* acid chloride see (2).]

Ba<sub>3</sub>A<sub>2</sub>.7H<sub>2</sub>O (from  $\bar{C}$  + BaCO<sub>3</sub> (2)), fairly eas. sol. cold aq. but spar. sol. in hot aq. (2). [ $\bar{C}$  on boilg. with aq. alkali does not give chloride ion (2) but  $\bar{C}$  with Zn + HCl (or H<sub>2</sub>SO<sub>4</sub>) or  $\bar{C}$  in 10 pts. aq. with 10 pts. 4.5% Na/Hg yields trimelic acid (1:0559) (2)]

**3:4975** (1) Davies, Wood, *J. Chem. Soc.* 1928, 1126-1127. (2) Ost, *J. prakt. Chem.* (2) **15**, 308-314 (1877).

**3:4978 2,3,5,6-TETRACHLOROBENZOQUINONE-1,4**  
(Tetrachloro-*p*-benzoquinone;  
chloranil)



$C_6O_2Cl_4$

Beil. VII - 636  
VII<sub>1</sub>-(347)

M.P. 292° (1) (68)  
291-292° (2)  
200° s.t. (3) (4) (5)  
290° (6) (7)  
289-200° (37)  
289° (60)  
288-290° (8)  
288° (9)  
285° (10)  
283-284° (11) (12)

[See also tetrachlorohydroquinone (3:4941).]

Golden-yellow *cryst.* from AcOH, acetone, C<sub>6</sub>H<sub>6</sub>, toluene, or by sublimation. — For crystallographic data see (13) (14) (15).

$\bar{C}$  on careful htg. sublimes without melting (16); for purification of  $\bar{C}$  by sublimation (4) under reduced press. (17) (18) see indic. refs.; for study of sublimation press. of  $\bar{C}$  see (19).

$\bar{C}$  is insol. aq.; alm. insol. in cold alc.; sparingly sol. hot alc. but somewhat more readily in ether;  $\bar{C}$  is sparingly sol. CHCl<sub>3</sub>, CCl<sub>4</sub>, CS<sub>2</sub>; insol. 1gr.

[For study of heat of formn. of  $\bar{C}$  see (20); for studies of heat of combustion see (21) (22).]

[For studies of bactericidal properties of  $\bar{C}$  (23) or toxicity of  $\bar{C}$  (or its associated by-products or contaminants) (24) (25) (26) see indic. refs.]

$\bar{C}$  comprises the essential constituent (99% (27)) of the commercial fungicide "Spergon" [for studies on use of  $\bar{C}$  as (seed) fungicide see (27) (28) (29) (30) (31) (32); for studies on toxicity of  $\bar{C}$  in such use see (33)].

### PREPARATION OF $\bar{C}$

$\bar{C}$  because of its great resistance to further oxidation is formed as the end product of the oxidation with  $HCl + KClO_3$  of a very large number of aromatic organic compounds [e.g., for a list of 16 such which do and 31 which do not give  $\bar{C}$ , see (34); for extension to 130 cases which do, see (35) cf. (36).]

$\bar{C}$  can also be prepared by a very large number of methods (see below): of these the best appear to be those from benzoquinone-1,4 (1:9025) using conc.  $HCl + 30\% H_2O_2$  at  $60^\circ$  (97% yield (37)) cf. (38), and from *p*-aminophenol by conversion with  $SO_2Cl_2$  (10 moles) at  $70^\circ$  (6) or at  $40-45^\circ$  for 4 days (73% yield (1)) to *N,N*-dichloro-2,3,5,6-tetrachloro-4-aminophenol, m.p.  $71.5^\circ$  (6), and reaction of the latter with boilg.  $EtOH$  (1) (6) in pres. of an inert solvent (39) to give (80-85% overall yield from *p*-aminophenol (1)) of  $\bar{C}$  of exceptional purity and free from 2,3,5-trichlorobenzoquinone-1,4 (3:4672).

### FROM VARIOUS PHENOLS

From phenol. [For prepn. of  $\bar{C}$  from phenol (1:1420) with conc.  $HNO_3 +$  fung.  $HCl$  (i.e., with aqua regia) on htg. in open flask in direct sunlight (25% yield (17)) (40), or in fung.  $HCl$  with  $Cl_2$  followed by htg. with conc.  $HNO_3$  at  $100^\circ$  for 20 hrs. (34% yield (17)) cf. (40), by electrolysis in  $HCl/AcOH$  (41), or by action of conc.  $HCl + KClO_3$  (42) (43) (note, however, that this method gives (17) (44) (45) (46) (47) a product seriously contaminated with 2,3,5-trichlorobenzoquinone-1,4 (3:4672) q.v.) see indic. refs. — For prepn. of  $\bar{C}$  from phenol-contg. industrial waste waters with  $Cl_2$  in alk. soln. followed by oxidn. with  $HNO_3$  see (48) (49) (50) (51) (52).]

From various halophenols. From 2,4,6-trichlorophenol. [For prepn. of  $\bar{C}$  from 2,4,6-trichlorophenol (3:1673) with  $ClSO_3H$  (53), with  $Cl_2 +$  fung.  $H_2SO_4$  followed by  $ClSO_3H$  (90% yield (54)), with aqua regia (17) (40), with  $HCl + KClO_3$  (42) (55), with  $CrO_3/AcOH$  (15), or with  $K_2Cr_2O_7/H_2SO_4$  (15) see indic. refs. — Note also that many of the processes starting from phenol (above) doubtless pass through 2,4,6-trichlorophenol.]

From pentachlorophenol. [For prepn. of  $\bar{C}$  from pentachlorophenol (3:4850) with  $ClSO_3H$  (53) (54), with cold fung.  $HNO_3$  (56) (57) (58), or with  $Cl_2 +$  conc.  $HCl$  at  $100^\circ$  (58) see indic. refs.]

From "hexachlorophenol." [For formn. of  $\bar{C}$  from "hexachlorophenol" (hexachlorocyclohexadien-1,4-one-3) (3:3180) with conc. (68) or fung. (69)  $HNO_3$ , with conc.  $H_2SO_4$  at  $100^\circ$  (68) (69), with aq. or  $HCl$  in s.t. at  $160^\circ$  (69), or with  $AlCl_3$  ( $\frac{3}{8}$  mole) in s.t. at  $160^\circ$  (70) see indic. refs.]

From 2,4,6-triiodophenol. [For prepn. of  $\bar{C}$  from 2,4,6-triiodophenol with  $Cl_2$  in boilg.  $AcOH$  soln. (100% yield) see (10).]

From various nitroso- and nitro-phenols. [For prepn. of  $\bar{C}$  from *p*-nitrosophenol in conc.  $HCl$  at  $90^\circ$  with  $Cl_2$  see (59).]

[For formn. of  $\bar{C}$  from *o*-nitrophenol (17) (40) (60), *p*-nitrophenol (17) (40) (60), 2,4,6-trinitrophenol (picric acid) (17) (40) (61) with aqua regia, or from picric acid with  $Cl_2$  (61) or  $Cl_2 + I_2$  (62) in hot aq. soln., or from picric acid with  $HCl + KClO_3$  (42) (47) see indic. refs.; for formn. of  $\bar{C}$  from *p*-nitrophenol or 2,4-dinitrophenol with aq.  $NaOCl$  soln. see (63).]

From polyhydric phenols. From *resorcinol*. [For formn. of  $\bar{C}$  from resorcinol (1:1530) with  $\text{ClSO}_3\text{H}$  (40 wt. pts.) at  $150\text{--}160^\circ$  for 25 hrs. (note that much 2,3,5-trichlorobenzoquinone-1,4 (3:4672) is also formed) see {64} cf. {51}.]

From *hydroquinone*. [For formn. of  $\bar{C}$  from hydroquinone (1:1590) with  $\text{Cl}_2$  in  $\text{AcOH}$  (5), with  $\text{Cl}_2$  + conc.  $\text{HCl}$  at  $100^\circ$  (65) {53}, with aqua regia (4), with  $\text{ClSO}_3\text{H}$  at  $150\text{--}160^\circ$  (8) see indic. refs.; for formn. of  $\bar{C}$  from hydroquinone-pyridinium chloride with  $\text{SOCl}_2$  (2) or from hydroquinone-2,6-bis-(sulfonyl chloride) with  $\text{PCl}_5$  in s.t. at  $140\text{--}150^\circ$  for 6 hrs. (67) see indic. refs.]

From *pyrogallol*. [For formn. of  $\bar{C}$  from pyrogallol (1 1555) with  $\text{ClSO}_3\text{H}$  at elevated temp. see {66} ]

From various quinones. From *p-benzoquinone*. [For formn. of  $\bar{C}$  from benzoquinone-1,4 (1.9025) with  $\text{Cl}_2$  in conc.  $\text{HCl}$  (53) {65} with  $\text{Cl}_2$  in  $\text{AcOH}$  (71) cf. {72}, or with  $\text{HCl}$  +  $\text{KClO}_3$  (42) see indic. refs.]

From the *dichloro-p-benzoquinones*. [For formn. of  $\bar{C}$  from 2,3-dichlorobenzoquinone-1,4 (3:2855), from 2,5-dichlorobenzoquinone-1,4 (3:4470), or from 2,6-dichlorobenzoquinone-1,4 (3:3750) with  $\text{Cl}_2$  in  $\text{CHCl}_3$  see {73}.]

From *trichloro-p-benzoquinone*. [For formn. of  $\bar{C}$  from 2,3,5-trichlorobenzoquinone-1,4 (3:4672) with  $\text{Cl}_2$  +  $\text{I}_2$  + aq. (47), or with  $\text{Cl}_2$  +  $\text{HCl}$  (65), see indic. refs.]

From various amines. [For formn. of  $\bar{C}$  from aniline in 10%  $\text{HCl}$  by electrolytic oxidation (23% yield (9)) (74), with  $\text{HCl}$  +  $\text{KClO}_3$  (75) (76), with  $\text{Na}_2\text{Cr}_2\text{O}_7$  +  $\text{HCl}$  (89), or with aqua regia (60) see indic. refs. — For formn. of  $\bar{C}$  from diphenylamine, 2,4-dichloroaniline, *m*-nitroaniline, aniline black, or phenylhydrazine with aqua regia see {60}.]

[For formn. of  $\bar{C}$  from *p*-phenylenediamine with aqua regia (60) (4), with  $\text{ClSO}_3\text{H}$  (large excess) at  $150\text{--}160^\circ$  for 5 hrs. (77), with  $\text{Cl}_2$  in  $\text{AcOH}$  (78), or with  $\text{HCl}$  +  $\text{KClO}_3$  (3) see indic. refs.; from 2,6-dichloro-*p*-phenylenediamine with  $\text{HCl}$  +  $\text{KClO}_3$  see {79}.]

[For formn. of  $\bar{C}$  from *o*-aminobenzoic acid (anthranilic acid) (42) (80), *m*-aminobenzoic acid (80), *p*-aminobenzoic acid (80), *L*-tyrosine ( $\alpha$ -amino- $\beta$ -(*p*-hydroxyphenyl)propionic acid) (81) with  $\text{HCl}$  +  $\text{KClO}_3$  see indic. refs.; from sulfanilic acid (aniline-*p*-sulfonic acid) with aqua regia see {60}.]

[For formn. of  $\bar{C}$  from 2,3,5,6-tetrachloro-*p*-phenetidine by diazotization and boilg. see {82}.]

From miscellaneous sources. [For formn. of  $\bar{C}$  from 1,2,4,5-tetrachlorobenzene (3:4115) as by-product of nitration with fuming  $\text{HNO}_3$  see under (3:4115); from hexachlorobenzene (3:4939) on boilg. with mixt. of fuming  $\text{HNO}_3$  + conc.  $\text{H}_2\text{SO}_4$  see {83}; from *N*-nitro-2,4,6-trichloroaniline in dil. alc. or  $\text{AcOH}$  soln. with  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  see {84}; from *N*-nitro-acet-2,3,5,6-tetrachloroaniline on boilg. in toluene or xylene see {85}; from tetrachlorobenzoquinone-1,4-mono-(2,4,6-trichlorophenylimide) by  $\text{H}_2\text{SO}_4$  hydrolysis see {86}; from various azo dyes by oxidn. with  $\text{NaOCl}$  soln. at  $0^\circ$  see {87}; from anisolesulfonic acid or phenetole-sulfonic acid in aq. soln. with  $\text{Cl}_2$  see {88}; from nitrobenzene with  $\text{ClSO}_3\text{H}$  (20 wt. parts) at  $150^\circ$  for 20 hrs. (95% yield) see {7} ]

## CHEMICAL BEHAVIOR OF $\bar{C}$

### REDUCTION OF $\bar{C}$

$\bar{C}$  upon reduction by a wide variety of reagents gives tetrachlorohydroquinone (3:4941) the text of which should be consulted for details.

### OXIDATION OF $\bar{C}$

$\bar{C}$  is extremely stable to oxidizing agents in neutral or acid soln. and is unaffected by aqua regia or hot conc.  $\text{HNO}_3$ .



## BEHAVIOR WITH CHLORINE

[ $\bar{C}$  with  $MnO_2$  + conc.  $HCl$  in s.t. at  $180^\circ$  for 10 hrs. adds 1 mole  $Cl_2$  giving (45) hexachlorocyclohexen-2-dione-1,4 [Beil. VII-574], m.p.  $89^\circ$  (45).]

## BEHAVIOR WITH OTHER INORGANIC REACTANTS

In many of the reactions of  $\bar{C}$  with other reagents, 2 of the chlorine atoms are often replaced by other groups as exemplified below.

With aqueous alkali.  $\bar{C}$  with dil. aq. alk. at  $70-80^\circ$  readily replaces 2 chlorine atoms by hydroxyls giving (16) (3) (00) (91) (92) 2,5-dichloro-3,6-dihydroxybenzoquinone-1,4 (chloranilic acid) (3:4970), m.p.  $282-284^\circ$  s.t. (92).

With ammonia. [ $\bar{C}$  with alc.  $NH_3$  on boilg. replaces 2 chlorine atoms by amino groups giving (75% yield (103)) (93) (94) 2,5-dichloro-3,6-diaminobenzoquinone-1,4 (chloroanilamide) [Beil. XIV-144]. — Note, however, that  $\bar{C}$  with aqueous  $NH_4OH$  gives (16) 2,5-dichloro-3-amino-6-hydroxybenzoquinone-1,4 (chloranilamic acid) [Beil. XIV-250].]

With various salts. [ $\bar{C}$  with sodium azide as directed (95) (96) gives 2,5-dichloro-3,6-bis-azidobenzoquinone-1,4. —  $\bar{C}$  with  $NaNO_2$  (2 moles) in conc. aq. soln. on warming gives (97) cf. (98) 2,5-dihydroxy-3,6-dinitrobenzoquinone-1,4 (nitranilic acid) [Beil. VIII-384, VIII-1-(683)]. —  $\bar{C}$  with  $KCN$  (2 moles) in 85%  $MeOH$  gives (99) 2,5-dihydroxy-3,6-dicyanobenzoquinone-1,4 (cyananilic acid) [Beil. XI-(520)].]

[ $\bar{C}$  with warm dilute aq. acid  $KHSO_3$  gives mainly (100) (101) the salt of 2,5-dichloro-3,6-disulfohydroquinone [Beil. XI-301], while with conc. solns. (100) or with neutral  $K_2SO_3$  (101) (102) the main prod. is the salt of thiochronic acid [Beil. XI-302, XI-(80)], now (102) recognized as cyclohexadien-2,5-di-4-one-1-pentasulfonic acid-2,3,4,5,6.]

With  $PCl_5$ . [ $\bar{C}$  with  $PCl_5$  +  $PCl_3$  in s.t. at  $190-200^\circ$  for 4 hrs. gives (05% yield (104)) cf. (43) hexachlorobenzene (3:4939); note also, however, that  $\bar{C}$  with  $PCl_5$  +  $PCl_3$  at  $135-140^\circ$  followed by treatment with aq. may also yield (45) (105) mono-(pentachlorophenyl)-phosphoric acid (monohydrate), m.p.  $224^\circ$  (105), and other products.]

BEHAVIOR OF  $\bar{C}$  WITH ORGANIC REACTANTS

With aromatic hydrocarbons. [ $\bar{C}$  with various aromatic hydrocarbons yields addition compounds: e.g.,  $\bar{C}$  with 1,2,4,5-tetramethylbenzene (durene) (1:7195) in hot  $AcOH$  gives (106) (107) a red cpd.  $\bar{C}$  2 durene;  $\bar{C}$  with hexamethylbenzene (1:7265) gives from hot  $AcOH$  (108) violet-brown ndls. of a 1:1 cpd., m.p.  $198-202^\circ$  (108) (for further study of this prod. see (109) (110));  $\bar{C}$  with acenaphthene (1:7225) gives (111) (112) from  $AcOH$  (107) a violet 1:1 addn. cpd.]

With dienes and other unsaturates.  $\bar{C}$  with many dienes and other highly unsaturated compounds forms addn. products and/or gives color reactions.

[ $\bar{C}$  with cyclopentadiene (1:8030) in  $C_6H_6$  in pres. of a little  $Me_3N$  gives (113) a 1:1 addn. cpd., yellowish ndls. from abs. alc., m.p.  $146-146.5^\circ$  (113) (corresp. dibromide with  $Br_2$  in  $CHCl_3$  in direct sunlight, lfts. from  $AcOEt$ , m.p.  $269^\circ$  (113)); note that in absence of  $Me_3N$  yield in 14 days is only 40%, in presence of  $Me_3N$  100% (for study of cat. influence of  $Me_3N$  and of  $CCl_3COOH$  see (114)).]

[For study of color reactions of  $\bar{C}$  in  $CHCl_3$  soln. with various trienes see (115) cf. (116) (117).]

[For studies of influence of  $\bar{C}$  on polymerization of styrene (1:7435) see (118) (119) (120); for study of effect of  $\bar{C}$  on polymerization or depolymerization of natural rubber see (121); for use of  $\bar{C}$  as vulcanization accelerator see (122).]

With organic OH (or SH) reactants. With alcohols. [ $\bar{C}$  in boilg.  $MeOH$  gradually treated with calcd. amt. 1%  $MeOH/KOH$  gives (123) (124) a mixt. of 2,5-dichloro-3,6-

dimethoxybenzoquinone-1,4 (chloranilic acid dimethyl ether) [Beil. VIII-380], dark red pr. from  $C_6H_6$ , m.p. 141–142° (123), and 2,6-dichloro-3,5-dimethoxybenzoquinone-1,4 (isochloroanilic acid dimethyl ether) [Beil. VIII-387], dark red pr., m.p. 159° (125) (126), 157–158° (123), 155.5° (127). — Note, however, that  $\bar{C}$  with MeOH/NaOMe (5–6 moles) gives 2,5-dichloro-3,6-dimethoxybenzoquinone-1,4-bis (monomethyl acetal) [Beil. VIII-381] accompanied by tetrachlorohydroquinone (3:4941).]

*With phenols.* [ $\bar{C}$  (1 mole) with phenol (2 moles) in aq. KOH at 100° gives (128) 2,5-dichloro-3,6-diphenoxybenzoquinone-1,4 (chloranilic acid diphenyl ether) [Beil. VIII-380], dark red pr. from  $C_6H_6$ , m.p. 243° (128). —  $\bar{C}$  (1 mole) with aq. K *p*-cresolate (2 moles) at 100° gives (129) 2,5-dichloro-3,6-di-(*p*-toloxy)benzoquinone-1,4 (chloranilic acid di-*p*-tolyl ether) [Beil. VIII-681)], cryst. from toluene, m.p. 254–255° (129) ]

*With mercaptans.* [ $\bar{C}$  (1 mole) with EtSH (4 moles) with EtOH/KOH (4 moles) as directed gives (95% yield (130)) 2,3,5,6-tetra-*kis*-(ethylthio)benzoquinone-1,4 [Beil. VIII-535], dark green ndls from alc., m.p. 90–91° (131).]

*With thiophenols.* [ $\bar{C}$  (1 mole) with  $C_6H_5SH$  in alk. soln. might be expected to yield 2,3,5,6-tetra-*kis*-(phenylmercapto)benzoquinone-1,4, but neither this reaction nor the expected product appears to have been reported. — However, various analogous cases are known: e.g.,  $\bar{C}$  (1 mole) with *p*-thiocresol (4 moles) in AcOH at 100° for  $\frac{1}{2}$  hr. gives (132) 2,3,5,6-tetra-*kis*-(*p*-tolylthio)benzoquinone-1,4, cryst. from AcOH, m.p. 203° (132). —  $\bar{C}$  (1 mole) with *o*-nitrothiophenol in boilg. EtOH for 1 hr. gives (96) 2,3,5,6-tetra-(*o*-nitrophenylmercapto)benzoquinone-1,4, no m.p. given.]

*With organic amines. General.* The behavior of  $\bar{C}$  with aliphatic amines appears to have been little studied from the structural viewpoint. [However, for studies on color reactions of  $\bar{C}$  with *prim.*, *sec.*, and *ter.*-amines (or their salts) (133), for use of  $\bar{C}$  (in epichlorohydrin soln.) as a test for plasmochin (134) (135), or for use of  $\bar{C}$  in detection of  $MeNH_2$ ,  $Me_2NH$ , or  $Me_3N$  and differentiation from  $NH_3$  (136) (137), for use in spot test reactions of 38 different amines (147) see indie. refs.]

*With primary aliphatic amines.* [ $\bar{C}$  with  $MeNH_2$  might be expected to give 2,5-dichloro-3,6-bis-(methylamino)benzoquinone-1,4 or even 2,3,5,6-tetra-*kis*-(methylamino)benzoquinone-1,4, but the reaction has not been reported and neither product is known.]

*With primary aromatic amines.* [ $\bar{C}$  with aniline in boilg. alc. refluxed 30 min gives (81% yield (138)) (100) (93) (139) 2,5-dichloro-3,6-dianilinobenzoquinone-1,4 [Beil. XIV-144, XIV-421)], yel.-hr. lfts. from  $C_6H_6$  or nitrobenzene, m.p. 292–293° (138), 290° (140), 288–290° (141); note that this product serves as bases for prepn. of many complex dyestuffs which cannot be discussed here. —  $\bar{C}$  with many other homologous and analogous primary aromatic amines behaves similarly.]

[ $\bar{C}$  with phenylhydrazine in absol. alc. evolves  $N_2$  and gives (10) a chlorine-contg prod., m.p. 229–230°, of undetermined structure.]

*With various organometallic reactants.* [ $\bar{C}$  (1 mole) in alc. with diethyl sodiomalonate (4 moles) in  $C_6H_6$  gives (10% yield (142)) tetraethyl 2,5-dichloro-*p*-benzoquinone-3,6-dimalonate [Beil. X-940], yel. ndls. from alc., m.p. 132° (143).]

[For behavior of  $\bar{C}$  with ethyl sodio-acetoacetate see (144) (145), Beil. X-860, and Beil. X-935 ]

[For behavior of  $\bar{C}$  with excess  $C_6H_5MgBr$  see (146).]

Ⓢ Color tests for  $\bar{C}$ . Of the large number of color tests shown by  $\bar{C}$  with various reactants, the following have been especially employed as preliminary tests for  $\bar{C}$  itself; note that for details, limitations, etc., the original references should be consulted.

*With dimethylaniline.*  $\bar{C}$  on warming with dimethylaniline gives intense violet color (Mulliken).

With ethyl cyanoacetate.  $\bar{C}$  with ethyl cyanoacetate (2-3 drops) + excess alc.  $\text{NH}_4\text{OH}$  (2-3 ml. of mixt. of 1 pt. abs.  $\text{EtOH}$  + 1 pt. conc.  $\text{NH}_4\text{OH}$ ) gives intense bluish-violet coloration, changing to blue, green, and finally reddish brown (148). [Note that the reaction is also shown by certain other quinones, e.g., benzoquinone-1,4 (1:9025),  $\alpha$ -toluquinone, thymoquinone, and naphthoquinone-1,4 (1:9040), but is not given by anthraquinone (1:9095), phenanthraquinone (1:9086), naphthoquinone-1,2 (1:9062), or 2,5-dichloro-3,6-diaminobenzoquinone-1,4 (chloranilamide) (148).]

With triphenylphosphine.  $\bar{C}$  with 20% soln. of  $(C_6H_5)_3P$  in  $CHCl_3$  gives (149) a wine-red color. [Note, however, that a similar behavior is also shown by 2,3,5-trichlorobenzoquinone-1,4 (3:4672) and certain other quinones (149).]

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(31) McNew, *Farm Research (Quart. Bull. N. Y. Agr. Expt. Sta.)* 8, No. 2, 9-11 (1942); *C.A.* 30, 3897 (1942). (32) McNew, *Farm Research (Quart. Bull. N. Y. Agr. Expt. Sta.)* 8, No. 2, 9-11 (1942); *C.A.* 30, 3897 (1942). (33) McNew, *Farm Research (Quart. Bull. N. Y. Agr. Expt. Sta.)* 8, No. 2, 9-11 (1942); *C.A.* 30, 3897 (1942). (34) McNew, *Farm Research (Quart. Bull. N. Y. Agr. Expt. Sta.)* 8, No. 2, 9-11 (1942); *C.A.* 30, 3897 (1942). (35) McNew, *Farm Research (Quart. Bull. N. Y. Agr. Expt. Sta.)* 8, No. 2, 9-11 (1942); *C.A.* 30, 3897 (1942).

Feb. 4, 1913; *Cent.* 1913, I 758; *C.A.* 7, 2096-2097 (1013).

(41) Fichter, Glantzstein, *Ber.* 49, 2473-2481 (1919). (42) Hoffmann, *Ann.* 52, 57-65 (1844).  
(43) Graebe, *Ann.* 146, 8-18 (1808). (44) Bouveault, *Ann. chim.* (8) 13, 142-144 (1908). (45)  
Zincke, Fuchs, *Ann.* 207, 15-19, (1892). (46) Knapp, Schultz, *Ann.* 219, 174-176 (1881).  
(47) Stenhouse  
*Ind. (U.S.S.R)*  
Shvedova, *Par*  
8386 (1938).

1974: 111-112

38. 1817-1821 (1919).

(61) Stenhouse, *Ann.* 99, 242 (1848). (62) Stenhouse, *Ann.* 145, 302-304 (1868). (63)



3:4989 4 CHLOROISOPHTHALIC ACID  
(4-Chlorobenzenedicarboxylic  
acid-1,3)



$C_8H_5O_4Cl$  Beil. IX - 837  
IX<sub>1</sub>-(372)

M.P. 205° (1)  
294.5° (2)  
203° (3)  
200-202° (4)  
280° u.c. (5)

Colorless ndls. from hot aq. in which it is very spar. sol. requiring 130 pts. for soln. (4); eas. sol. alc., spar. sol. ether; insol.  $C_2H_5$  or  $CHCl_3$  (2).

[For prepn. of  $\bar{C}$  from 4-chloro-1,3-dimethylbenzene (3:8665) by oxidn. with aq.  $KMnO_4$  (1) in pres. of  $MgSO_4$  (2) see indic. refs.; from 2-chloro-5-methylphenyl methyl ketone (3), 2-chloro-5-methylbenzoic acid (6) (3:4615), or  $\alpha,\beta$ -bis-(2-chloro-5-methylbenzoyl)ethylene (5) by oxidn. with  $KMnO_4$  see indic. refs.; from sodium 1,3-dimethylbenzenesulfonate [Beil. XI-123, XI<sub>1</sub>-(34)] with  $SOCl_2$  in s.t. at 230°, followed by treatment with aq. alk., see (7); from 4-chloroisophthaldiamide (see below) by hydrolysis with boilg. aq.  $KOH$  see (4).]

— Dimethyl 4-chloroisophthalate: unreported.

— Diethyl 4-chloroisophthalate: unreported.

— 4-Chloroisophthaldiamide: ndls., lfts., or pl. from 17 pts. boilg. aq., m.p. 232-233° (4). [From isophthalic acid-4-arsinic acid (1,3-dicarboxybenzenearsinic acid-4, 1,3  $(HOOC)_2.C_6H_3.As(O)(OH)_2$ , with  $PCl_5$  at 110° for 3 hrs. followed by treatment in toluene soln. with  $NH_3$  (4).]

3:4980 (1) Davies, Wood, *J. Chem. Soc.* 1928, 1126. (2) Ullmann, Uzbachian, *Ber.* 36, 1799 (1903). (3) Mayer, Freund, *Ber.* 55, 2052 (1922). (4) Gough, King, *J. Chem. Soc.* 1930, 690-691. (5) Conant, Lutz, *J. Am. Chem. Soc.* 47, 891 (1925). (6) Scholl, Meyer, Keller, *Ann.* 513, 208 (1934). (7) Farbwerke Meister Lucius & Brüning, Ger. 282,133, Feb. 15, 1915; *Cent.* 1915, I 464.

3:4985 2,5-DICHLOROTEREPHTHALIC ACID  
(2,5-Dichlorobenzenedicarboxylic  
acid-1,4)



$C_8H_4O_4Cl_2$  Beil. IX - 847  
IX<sub>1</sub>—

M.P. 306-306.5° (1)  
305-306° cor. (2)  
305° (3)

Colorless ndls. from hot aq.; sublimes on cautious gradual htg.

[For prepn. of  $\bar{C}$  from 2,5-dichloro-1-methyl-4-isopropylbenzene (2,5-dichloro-*p*-cymene [Beil. V-423, V<sub>2</sub>-(326)] by oxidn. with 20 pts.  $HNO_3$  ( $D = 1.15$ ) in s.t. at 180-200° for 10-12 hrs. (1) (3) see indic. refs.; from 2,5-dichlorocyclohexadiene-1,4-dicarboxylic acid-1,4 (2,5-dichloro-3,6-dihydroterephthalic acid) [Beil. IX-785] in 12% yield by short boilg. with 20%  $HNO_3$  (some 2,5-dichloro-3-nitroterephthalic acid is also formed) see (4) (2); from 2,5-dichloro-1,4-bis-(trichloromethyl)benzene (5) by hydrolysis with  $H_2SO_4$  (66° B $\bar{e}$ ) at 70-80° see (5).]

$\frac{1}{\sqrt{e}}$  44 2 34 4-9 20

3:4990 (1) Klingstedt, *Wiss. Ber. d. k. k. Hof- u. allg. med. ch. Anst. Wien*, 1891, 1: 504; *Cent.* 1928, I 504; 2104 (1931). (3) 1  
*Sci. Kyoto Imp. Un.*  
 Nörr, *Ber.* 33, 726  
 Hendrick, Billicke,  
 Linden, *Ber.* 45, 2  
 Matthews, *J. Chem. Soc.* 69, 165-172 (1891).

3:4995 **CHLOROTEREPHTHALIC ACID**  
 (2-Chlorobenzenedicarboxylic  
 acid-1,4)


 $C_8H_5O_4Cl$ 

Beil. IX-847  
 IX<sub>1</sub>—

M.P. 320° (1) (2)  
 Above 300° (3)  
 300° (4)

Cryst. from hot aq. (3), very dil. alc., (3) or 50% alc. (7); sol. in much hot aq., eas. sol. alc. or ether.

[For prepn. of  $\bar{C}$  from 2-aminobenzenedicarboxylic acid-1,4 [Beil. XIV-558, XIV<sub>1</sub>-(637)] via diazotization and use of  $Cu_2Cl_2$  reactn. see (3); from 3-chloro-1-methyl-4-isopropylbenzene (3-chloro-*p*-cymene) (3:8770) by oxidn. with 15 pts. boilg.  $HNO_3$  ( $D = 1.39$ ) for 1 day (other prods. are also formed) see (4); from 3-chloro-4-acetylbenzoic acid (1), from 2-chloro-4-acetylbenzoic acid (2), or from 3-chloro-4-methylphenyl methyl ketone (8) by oxidn. with alk.  $KMnO_4$  see indic. refs.; from 2-chloro-4-carbamidobenzoic acid (5) by hydrolysis with boilg. 25%  $NaOH$  see (5); from 2-chloro-4-methylbenzotrichloride (6) by hydrolysis with  $H_2SO_4$  (66° B $_4$ ) at 70-80° see (6).]

$Ag_2\bar{A}$ ; pptd. from soln. of  $(NH_4)_2\bar{A}$  by addn. of  $AgNO_3$  (3).

[ $\bar{C}$  with  $PCl_5$  (3) or with  $SOCl_2$  in pres. of  $SbCl_5$ ,  $AlCl_3$ , or  $SnCl_4$  (7) yields chloroterephthaloyl (di)chloride, b.p. 154-155° at 19 mm. (7).]

[ $\bar{C}$  on nitration with  $HNO_3/H_2SO_4$  at 65° yields (7) 2-chloro-5-nitrobenzenedicarboxylic acid-1,4, cryst. from 50% alc., m.p. 265° (7), 263-264° (8) (this prod. is also obtd. from 2-chloro-4-methyl-5-nitrophenyl methyl ketone (8) by oxidn.).]

① Dimethyl chloroterephthalate: lfts. from  $MeOH$ , m.p. 60° (6) (3), 59-60° (4). [From  $\bar{C}$  in  $MeOH$  with  $HCl$  gas or from  $Ag_2\bar{A}$  with  $MeI$  (3).]

— Diethyl chloroterephthalate: oil (3).

— Chloroterephthaldiamide: cryst. from dil. alc., m.p. above 300° (3). [From chloroterephthaloyl (di)chloride (above) with  $(NH_4)_2CO_3$  (3).]

3:4995 (1) Ganguly, LeFevre, *J. Chem. Soc.* 1934, 851. (2) Ganguly, LeFevre, *J. Chem. Soc.* 1934, 854. (3) Ahrens, *Ber.* 19, 1637-1639 (1886). (4) Fileti, Cross, *Gazz. chim. ital.* 18, 11 311, 313 (1888). (5) Magidson, Trawin, *Ber.* 69, 540 (1936). (6) I.G., French 663,791, Aug. 26, 1929; *Cent.* 1929, II 2731-2732. (7) I.G., French 810,595, March 24, 1937; *Cent.* 1937, I 5048; *C.A.* 32, 592 (1938). (8) Mayer, Albert, Schön, *Ber.* 65, 1296, 1298-1299 (1932).

# CHAPTER XII

## DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

### Section 1. $D_4^{20}$ greater than 1.1500

(1.15000-1.15100)

1.15000 PHOSPHENE

(distillation residue)

$OM_2$

$Bo. III = 13$

$III_1(7)$

$III_2(12)$

BP	FP
$8.2^{\circ}C$ at 716 mm. (1)	$-118^{\circ}C$ (1) $D_4^{20} = 1.1392$ (1)
$8.5^{\circ}C$ at 716 mm. (2)	$-126^{\circ}C$ (1)
$8.1^{\circ}C$ at 716 mm. (3)	$-127.5^{\circ}C$ (1) (see p. 267)
$8.07^{\circ}C$ at 716 mm. (4)	$-128^{\circ}C$ (1)
$7.95^{\circ}C$ at 716 mm. (1)	
$7.94^{\circ}C$ at 716 mm. (4)	
$8.06^{\circ}C$ at 716 mm. (1)	

(see p. 267)

1.15000-1.15100. The boiling point of the sample was  $8.2^{\circ}C$  at 716 mm. (1) and  $8.5^{\circ}C$  at 716 mm. (2). The freezing point was  $-118^{\circ}C$  (1) and  $-126^{\circ}C$  (1). The density was  $1.1392$  (1) at  $20^{\circ}C$ . The refractive index was  $1.3412$  (1) at  $20^{\circ}C$ . The sample was a colorless liquid with a strong odor of phosphorus.

1.15000-1.15100. The boiling point of the sample was  $8.1^{\circ}C$  at 716 mm. (3) and  $8.07^{\circ}C$  at 716 mm. (4). The freezing point was  $-127.5^{\circ}C$  (1) and  $-128^{\circ}C$  (1). The density was  $1.1392$  (1) at  $20^{\circ}C$ . The refractive index was  $1.3412$  (1) at  $20^{\circ}C$ . The sample was a colorless liquid with a strong odor of phosphorus.

1.15000-1.15100. The boiling point of the sample was  $7.95^{\circ}C$  at 716 mm. (1) and  $7.94^{\circ}C$  at 716 mm. (4). The freezing point was  $-128^{\circ}C$  (1). The density was  $1.1392$  (1) at  $20^{\circ}C$ . The refractive index was  $1.3412$  (1) at  $20^{\circ}C$ . The sample was a colorless liquid with a strong odor of phosphorus.

1.15000-1.15100. The boiling point of the sample was  $8.06^{\circ}C$  at 716 mm. (1). The freezing point was  $-128^{\circ}C$  (1). The density was  $1.1392$  (1) at  $20^{\circ}C$ . The refractive index was  $1.3412$  (1) at  $20^{\circ}C$ . The sample was a colorless liquid with a strong odor of phosphorus.

1.15000-1.15100. The boiling point of the sample was  $8.2^{\circ}C$  at 716 mm. (1) and  $8.5^{\circ}C$  at 716 mm. (2). The freezing point was  $-118^{\circ}C$  (1) and  $-126^{\circ}C$  (1). The density was  $1.1392$  (1) at  $20^{\circ}C$ . The refractive index was  $1.3412$  (1) at  $20^{\circ}C$ . The sample was a colorless liquid with a strong odor of phosphorus.

1.15000-1.15100. The boiling point of the sample was  $8.1^{\circ}C$  at 716 mm. (3) and  $8.07^{\circ}C$  at 716 mm. (4). The freezing point was  $-127.5^{\circ}C$  (1) and  $-128^{\circ}C$  (1). The density was  $1.1392$  (1) at  $20^{\circ}C$ . The refractive index was  $1.3412$  (1) at  $20^{\circ}C$ . The sample was a colorless liquid with a strong odor of phosphorus.

1.15000-1.15100. The boiling point of the sample was  $7.95^{\circ}C$  at 716 mm. (1) and  $7.94^{\circ}C$  at 716 mm. (4). The freezing point was  $-128^{\circ}C$  (1). The density was  $1.1392$  (1) at  $20^{\circ}C$ . The refractive index was  $1.3412$  (1) at  $20^{\circ}C$ . The sample was a colorless liquid with a strong odor of phosphorus.



solvents at pressures below 1 atm. see (32) cf. (33); for patent on removal of  $\bar{C}$  from contaminated drinking water by extraction with org. solvents see (34)].

[For technical papers (36) (37) (38) (39) (40) (41) (42) (43) (44) (45) and patents (46) on adsorption of  $\bar{C}$  by various forms of carbon see indic. refs.]

[For influence of  $\bar{C}$  in extinction of H/O flames see (47).]

### PHYSIOLOGICAL ASPECTS OF $\bar{C}$

$\bar{C}$  is more than ten times as toxic as  $Cl_2$ . An atmosphere contg. 1 part by vol. of  $\bar{C}$  in 6000 may cause lung injuries in 2 min., 1 part in 30,000 is very dangerous, and 1 part in 200,000 is probably fatal for exposures of 30 min. The maximum permissible concn. for prolonged exposure is about 1 p.p.m., i.e., 0.004 mg./l. (48).

The least detectable odor of  $\bar{C}$  is 5.6 p.p.m., the least concn. that affects the throat is 3.1 p.p.m., the least concn. that causes irritation of the eyes is 4.0 p.p.m., the least concn. that causes coughing is 4.8 p.p.m. (48) (49). A concn. of 0.02-0.05% is lethal to most animals in a short time, a concn. of 0.0025% is dangerous for exposures of 30-60 min., and the maximum concn. to which animals can be exposed for several hours without serious effects is 0.0001% or 1 p.p.m. (48) (50).

[For report of industrial accidents from  $\bar{C}$  (51), for legal (British) aspects of industrial poisoning by  $\bar{C}$  (52), for toxicology and treatment of poisoning by  $\bar{C}$  (53), for immunization against  $\bar{C}$  (54), for variations in toxicity of  $\bar{C}$  for small animals with duration of exposure (55) see indic. refs.]

[For studies relating to chemical warfare aspects of  $\bar{C}$  with respect to foodstuffs see (56) (57).]

### USES OF $\bar{C}$

Apart from the uses of  $\bar{C}$  as a chemical warfare agent (above), many chemical utilizations are indicated below under its chemical behavior. (In addition will be mentioned here a few further examples as follows: for use of mixt. of  $\bar{C}$  + HF for cracking of hydrocarbon oils see (58); for use as dehydrating agent in conversion of amides to corresp. nitriles see (59); for use in sepn. of Pt metals see (60).]

### DETECTION OF $\bar{C}$

$\bar{C}$  may be detected by its characteristic odor (see above) and by various color reactions of which the following represent the more important types.

For detection of  $\bar{C}$  by the yellow or orange color produced by reaction with Harrison's reagent (a soln. in EtOH (100 ml.) of *p*-dimethylaminobenzaldehyde [Beil. XIV-31, XIV-1-360]) (5 g.) (for prepn. see (61)) and of diphenylamine [Beil. XII-174, XII-1-163]) (5 g.) see (62) (63) (64) (65) (66) (67) (68) (69) (70) (71) (83); note that this test suffers interference from HCl,  $Cl_2$ ,  $ClSO_3H$ ,  $TiCl_4$ , chloromethyl chloroformate (3:5275), diphosgene (3:5515), and triphosgene (3:1915); for application of this reagent in an absorptive tube see (72) cf. (73).

For detection of  $\bar{C}$  by green color imparted to a test paper impregnated with a xylene soln. of 0.5% 6-nitroso-3-dimethylaminophenol (4-dimethylamino-*o*-benzoquinoneoxime-1) [Beil. XIV-131] and a xylene soln. of 0.5% *m*-diethylaminophenol [Beil. XIII-408, XIII-1-130]) see (74) (75) (76).

For spot test detection of  $\bar{C}$  by use of phenylhydrazine cinnamate (for prepn. see (77)) in  $CHCl_3$  or  $CCl_4$  followed by treatment with 1%  $CuSO_4$  soln. to give a red-violet color from the 1,5-diphenylcarbohydrazide [Beil. XV-292, XV-1-72]) produced see (78).

For study of detection of  $\bar{C}$  with resorcinol (1:1530) or vanillin (1:0050) see (79); by

indirect use of the Gilman color test for  $\text{RMgX}$  compounds see (80) cf. (81); for study of utility of various dyestuffs in detection of  $\bar{\text{C}}$  see (82).

### DETERMINATION OF $\bar{\text{C}}$

Methods for the quant. detn. of  $\bar{\text{C}}$  may be classified under three main types according to whether they are based upon hydrolysis, reaction with alkali iodides, or reaction with aniline.

Detn. by methods based on hydrolysis. (For studies of methods based upon alkaline hydrolysis of  $\bar{\text{C}}$  and subsequent detn. of resultant chloride ion see (83) (84) (85) (86) (87) (88) (89) (90); for especial criticism of this method see (91).]

Detn. by reaction with alkali iodide. [For studies of methods based upon reaction of  $\bar{\text{C}}$  with  $\text{NaI}$  (92) (91) or  $\text{KI}$  (93) in acetone followed by thiosulfate titration of the liberated  $\text{I}_2$  see indic. refs.]

Detn. by reaction with aniline. [For study of methods based upon reaction of  $\bar{\text{C}}$  with aniline and gravimetric estn. of the resultant  $N,N'$ -diphenylurea (carbanilide) (94) (95) cf. (91) or titration of the residual aniline  $\text{HCl}$  in the filtrate (96) see indic. refs.]

Related topics. [For detn. of small amts.  $\text{Cl}_2$  in pres. of  $\bar{\text{C}}$  (97), of  $\text{HCl}$  in  $\bar{\text{C}}$  (98) (85), for analysis of mixts. of  $\bar{\text{C}}$  +  $\text{Cl}_2$  +  $\text{NOCl}$  (99), for anal. of mixts. of  $\bar{\text{C}}$  with  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$ ,  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_6$  (88) (86), for anal. of industrial  $\bar{\text{C}}$  (89), or for detn. of  $\bar{\text{C}}$  in air by means of an ultraviolet photometer (R. + H. Tri-Per Analyzer) (100) see indic. refs.]

### PREPARATION OR FORMATION OF $\bar{\text{C}}$

From  $\text{CO} + \text{Cl}_2$ . The photochemical reaction of  $\text{CO}$  with  $\text{Cl}_2$  to yield  $\bar{\text{C}}$  was the method by which it was first prepared in 1812 (9) (for extensive history see (10)). Over the years the reaction has been very extensively studied. The more important earlier reports include those of Wilm and Wischin (101), Wildermann (102), Dyson and Hardin (103), Weigert (104), Coehn and Becker (105), Chapman and Gee (106), etc. Since 1920 the number of studies of this reaction has so greatly increased as to preclude in this text any detailed analysis; however, the following references ((107)-(134), incl.) arranged in receding chronology will be found fruitful from one viewpoint or another.

[For studies on formn. of  $\bar{\text{C}}$  from  $\text{CO} + \text{Cl}_2$  in dark at  $349-452^\circ$  (135) in liq. medium (145), or over cat. such as  $\text{Pt}$  at  $300-400^\circ$  (136), activated carbon (6) (137), or  $\text{AlCl}_3$  at  $30-35^\circ$ , or in  $\text{CHCl}_3$  soln. (138) see indic. refs. — For formn. of  $\bar{\text{C}}$  from  $\text{CO} + \text{NOCl}$  over activated carbon at  $100-250^\circ$  see (139) cf. (137).]

[For formn. of  $\bar{\text{C}}$  from  $\text{CO}$  passed over heated  $\text{AgCl}$  (140) (141), over  $\text{CuCl}_2$ ,  $\text{PbCl}_2$ , or  $\text{NiCl}_2$  at  $450-750^\circ$  (141), over heated  $\text{AuCl}_3$  (142), or through boilg.  $\text{SbCl}_3$  (143), or over chlorides of Pt metals (144) see indic. refs.]

From various chlorinated hydrocarbons. From  $\text{CCl}_4$ . [For studies on formn. of  $\bar{\text{C}}$  from  $\text{CCl}_4$  (3:5100) during use of latter as fire extinguisher see (146) (84) cf. (147) (368); for patents on repression of formn. of  $\bar{\text{C}}$  in such use see (148) (149) (150) cf. (368); for formn. of  $\bar{\text{C}}$  from  $\text{CCl}_4$  fire extinguishers on  $\text{Mg}$  see (151); for phosgene content of smoke from Berger mixt. ( $\text{Zn} + \text{chlorohydrocarbons}$ ) see (152).]

[For formn. of  $\bar{\text{C}}$  from  $\text{CCl}_4$  with  $\text{O}_2$  in light of  $2537 \text{ \AA}$  (153) or with atomic oxygen (154) see indic. refs.]

[For formn. of  $\bar{\text{C}}$  from  $\text{CCl}_4$  by chemical oxidizing agents such as  $\text{O}_2$  over white-hot  $\text{Pt}$  (155), air over  $\text{CuCl}_2$  or  $\text{FeCl}_3$  at elev. temp. (156),  $\text{GeO}_2$  (157), chromic acid (1) (158), pyrosulfuryl chloride (1 mole) + sulfuric acid monohydrate (2 moles) on warming (158) (159) (160) (161) (162) (163) see indic. refs.]

[For formn. of  $\bar{\text{C}}$  from  $\text{CCl}_4$  by passing with  $\text{CO}_2$  over pumice at  $350^\circ$  (161), by htg. with

ZnO at 200° (164), with P<sub>2</sub>O<sub>5</sub> at 200–220° for 2 days (165), or over gypsum at 900° (166), or even by htg. with a little aq. in s.t. at 250° (220) see indic. refs.]

*From CHCl<sub>3</sub>.* [For an extensive account of formn. of  $\bar{C}$  from CHCl<sub>3</sub> (3:5050) by oxidn. in air and light see (167). Note that such oxidn. is not effected by air in absence of light, nor by light in absence of air (168). With limited air in sunlight CHCl<sub>3</sub> reacts according to equation  $\text{CHCl}_3 + \text{O} \rightarrow \text{COCl}_2 + \text{HCl}$ , but with excess air in sunlight in sense  $2\text{CHCl}_3 + 5\text{O} \rightarrow 2\text{CO}_2 + 3\text{Cl}_2 + \text{H}_2\text{O}$  (169). Note that CHCl<sub>3</sub> + air over dry KOH gives some  $\bar{C}$  (170). For studies on photochem. oxidn. of CHCl<sub>3</sub> (171) in tropical sunlight (172) including search for possible intermediate peroxides (173) (174) see indic. refs. For studies of Cl<sub>2</sub>-sensitized photochem. oxidn. of CHCl<sub>3</sub> see (175) (176) (177). For oxidn. of CHCl<sub>3</sub> by atomic oxygen see (154).]

[For formn. of  $\bar{C}$  from CHCl<sub>3</sub> (3:5050) by shaking with siloxen + excess O<sub>2</sub> (178), by action of O<sub>3</sub> (179) (180), by passing over CuO at 350–550° (181) or gypsum at 900° (166), with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>SO<sub>4</sub> (1) (158), with ClSO<sub>3</sub>H at 120° (187), or during explosion of CHCl<sub>3</sub> with alkali metals (182) see indic. refs.]

*From Cl<sub>2</sub>C=CCl<sub>2</sub>.* [For formn. of  $\bar{C}$  from tetrachloroethylene (3:5460) during Cl<sub>2</sub>-sensitized photochem. oxidn. see (183) (184) (185).]

*From Cl<sub>2</sub>C=CHCl.* [For formn. of  $\bar{C}$  from trichloroethylene (3:5170) with air or O<sub>2</sub> see (186).]

*From various compounds containing the trichloromethyl group.* [For formn. of  $\bar{C}$  from trichloroacetaldehyde (ehloral) (3:5210) by Cl<sub>2</sub>-sensitized (188) or Br<sub>2</sub>-sensitized (189) photochem. oxidn. with O<sub>2</sub> at 70–90°, with Cl<sub>2</sub> in sunlight (190), or with AlCl<sub>3</sub> on warming (191) see indic. refs.]

[For formn. of  $\bar{C}$  from trichloroacetic acid (3:1150) on htg. with ZnCl<sub>2</sub> (192), on illuminating dry acid in pres. of air (193), or on electrolysis of aq. soln. (194) see indic. refs.; from trichloroacetyl chloride (3:5420) at 600° (195); from trichloroacetonitrile in air (196); from trichloroacetyl hydrogen peroxide on warming (200); from trichlorobromomethane + Br<sub>2</sub> + O<sub>2</sub> in light (197) see indic. refs.]

[For formn. of  $\bar{C}$  from di-(trichloromethyl) carbonate (triphosgene) (3:1915) on distn. (198), htg. at 200° in s.t. (199), or on mixing with charcoal and htg. just above m.p. (78°) (198) see indic. refs.; from trichloromethyl ehloroformate (diphosgene) (3:5515) on htg. above 300° (200) (209) or on contact with activated carbon, charcoal, or iron oxide at ord. temp. (198); from methyl trichloromethyl carbonate [Beil. III-17, III-(8), III-(15)], h.p. 57–58° at 17 mm. (204),  $D_4^{17} = 1.5228$  (204),  $n_D^{17} = 1.4487$  (204), on hoilg. at ord. press. (202) or on warming with AlCl<sub>3</sub> (203) (204); from ethyl trichloromethyl carbonate, h.p. 78° at 19 mm. (204),  $D_4^{20} = 1.4205$  (204),  $n_D^{20} = 1.4450$  (204), or from *n*-propyl trichloromethyl carbonate, h.p. 93° at 12 mm. (204),  $D_4^{20} = 1.359$  (205),  $n_D^{20} = 1.4451$  (205), on warming with AlCl<sub>3</sub> (203); from isoamyl trichloromethyl carbonate, h.p. 120° at 23 mm. (204),  $D_4^{20} = 1.2644$  (204),  $n_D^{20} = 1.4466$  (204), phenyl trichloromethyl carbonate [Beil. VI-(88)], m.p. 70.5° (204), or *p*-tolyl trichloromethyl carbonate (206) on warming with aq. (but not with aq. NaOH) (206); from *bis*-(trichloromethyl) oxalate [Beil. III-17] at 350–400° (207); or from trichloromethyl perchlorate (208) see indic. refs.]

[For formn. of  $\bar{C}$  from trichloronitromethane (chloropicrin) [Beil. I-76, I-(20), I-(41)] in u.v. light (210), on hoilg. (at 112°) under ord. press. (211), on passing with HCl over pumice at 400° (212), or on treatment with fuming H<sub>2</sub>SO<sub>4</sub> (20% SO<sub>3</sub>) at 100° (213) see indic. refs.]

*From miscellaneous sources.* [For formn. of  $\bar{C}$  from CO<sub>2</sub> + CCl<sub>4</sub> (3:5100) + cat. at elevated temp. (225), from CS<sub>2</sub> with aqua regia (214) or Cl<sub>2</sub>O (215); from COS with Cl<sub>2</sub> at red heat (1); from COS over fused CuCl<sub>2</sub> (1) or through hoiling SbCl<sub>5</sub> (1); from thiophosgene with air or O<sub>2</sub> under various conditions (216); from anhydrous Na<sub>2</sub>CO<sub>3</sub> with

$\text{PCl}_5$  (217); from pentachloropropionyl chloride (3:0470) with  $\text{AlCl}_3$  at  $60^\circ$  (218); from oxalyl (di)chloride (3:5060) at  $600^\circ$  or with  $\text{AlCl}_3$  in  $\text{CS}_2$  on warming (219) see indie. refs.]

## CHEMICAL BEHAVIOR OF $\dot{\text{C}}$

Pyrolysis of  $\dot{\text{C}}$ .  $\dot{\text{C}}$  on heating above  $300^\circ$  decomposes in two ways: (1) into  $\text{CO} + \text{Cl}_2$  ( $\text{CO}$  equilibrium) and (2) into  $\text{CO}_2 + \text{CCl}_4$  ( $\text{CO}_2$  equilibrium). The extent of these reactions together with the influence of various factors has been extensively studied. [For a concise summary of earlier work see the review of Dyson (11); for many important details see the original references represented by (225) (221) (222) (5) (135) (6) (223) (224).]

Photochemical decompn. of  $\dot{\text{C}}$ . [ $\dot{\text{C}}$  on exposure to short-wave u.v. light decomposes yielding (105) (226)  $\text{CO} + \text{Cl}_2$ ; for more recent studies of this photochem. decompn. see (227) (228) (229) (230) (231); for application to problem of separation of isotopes of  $\text{Cl}_2$  see (232).]

Electrolysis of  $\dot{\text{C}}$ . [ $\dot{\text{C}}$  or a soln. of  $\text{AlCl}_3$  in  $\dot{\text{C}}$  upon electrolysis gives (233)  $\text{CO} + \text{Cl}_2$ ]

## BEHAVIOR OF $\dot{\text{C}}$ WITH INORGANIC REACTANTS

Reduction of  $\dot{\text{C}}$ . [ $\dot{\text{C}}$  +  $\text{H}_2$  in u.v. light at  $10^\circ$  gives  $\text{CO} + \text{HCl}$  + traces of formaldehyde (1:0145) but at  $80^\circ$  gives  $\text{CO} + \text{CO}_2 + \text{CH}_4 + \text{HCl}$  (234). —  $\dot{\text{C}}$  +  $\text{H}_2$  over Pd or Ni on pumice, or over vanadium carbide, at  $300\text{--}450^\circ$  gives (235) cf. (236)  $\text{CO} + \text{HCl}$  + small amts. formaldehyde (1:0145) cf. (229).]

Oxidation of  $\dot{\text{C}}$ . [For study of photochem. oxidn. of  $\dot{\text{C}}$  see (230).]

Hydrolysis of  $\dot{\text{C}}$ . Contrary to earlier reports  $\dot{\text{C}}$  with aq. is almost instantly hydrolyzed but the rate is influenced by the manner in which contact is effected and whether the aq. is in vapor or liquid state. [For studies on the hydroly. of  $\dot{\text{C}}$  see (237) (4) (96) (238); for study of rate of hydrolysis in dioxane at  $25^\circ$  (239) or in toluene at  $25^\circ$  and at  $45^\circ$  (240) see indie. refs.]

Behavior of  $\dot{\text{C}}$  with metal oxides, sulfides, or phosphates. [ $\dot{\text{C}}$  with metallic oxides on htg. at  $250\text{--}600^\circ$  (depending upon the metal) gives the corresp. metal chloride which in some cases, e.g.,  $\text{FeCl}_3$ ,  $\text{ThCl}_4$ , readily sublimes in pure form; for examples of this reaction see (211) (212) (213); for use in prepn. of  $\text{AlCl}_3$  see (219).]

[ $\dot{\text{C}}$  on htg. with metal sulfides gives (216)  $\text{COS}$  [Boil. III-131, III<sub>2</sub>-(61), III<sub>2</sub>-(101)], b.p.  $-50.2^\circ$  (211), f.p.  $-138.2^\circ$  (214) (use with  $\text{CdS}$  in prepn. (215)), and the metal chloride cf. (211).]

[ $\dot{\text{C}}$  on htg. with certain phosphates (217) gives  $\text{CO}_2 + \text{POCl}_3$  + metal chloride (use in prepn. of  $\text{POCl}_3$  (218)).]

Analogs of  $\dot{\text{C}}$ . *Carbonyl fluoride*. [This compound, b.p.  $-83.1^\circ$  (250), m.p.  $-114.0^\circ$  (250), has been prepd. from  $\text{AgF}_2 + \text{CO}$  (250),  $\text{F}_2 + \text{CO}$  (251) cf. (250), or from acetone with  $\text{F}_2$  (252), but has not been reported from  $\dot{\text{C}}$ . Note that  $\dot{\text{C}}$  with  $\text{HF}$  at  $80^\circ$  and 250 Hg. eq. in. in  $\text{Cu}$  bomb gives (25-50% yield (253)) carbonyl chlorofluoride,  $\text{COClF}$ , b.p.  $-42^\circ$ , m.p.  $138^\circ$  (253).]

*Carbonyl bromide*. [ $\dot{\text{C}}$  with  $\text{HBr}$  at  $150^\circ$  (254) or with  $\text{AlBr}_3$  (255) gives carbonyl bromide [Boil. III-29, III<sub>2</sub>-(9), III<sub>2</sub>-(7)], but this prod. is better prepd. from  $\text{CBr}_4$  by oxidn. with conc.  $\text{H}_2\text{SO}_4$  (256) (257) (258) (for study of photochemical oxidn. see (259)); for studies of structure (26) and pyrolysis (260) (261) (262) see indie. refs.]

*Carbonyl cyanide*. [This compound, b.p.  $65.0\text{--}65.5^\circ$  (263),  $d_4^{25} = 1.124$  (263),  $n_D^{25} = 1.2019$  (263), has been prepd. from acetone- $\alpha$ -chloroethyl ester (1:0145) by conversion (264) to di- $\alpha$ -chloroacetone [Boil. I-266, I<sub>2</sub>-(413)], thence to diacetyl-dichloroacetone (265), then acetone- $\alpha$ -acetyl cyanide (267) which was then pyrolyzed at  $160\text{--}165^\circ$  and

210–220 mm. (263) cf. (265). For formn. using propionyl (instead of acetyl) derivatives see (266).]

Behavior of  $\bar{C}$  with inorganic acids. [ $\bar{C}$  with HF as directed (250) (see analogs of  $\bar{C}$  above) gives carbonyl chlorofluoride. —  $\bar{C}$  with HBr does not react even at 200° (267). —  $\bar{C}$  as liq. does not react with HI, but  $\bar{C}$  as gas reacts with HI gas even at room temp. with sepn. of  $I_2$  (267).]

Behavior of  $\bar{C}$  with inorganic salts. [ $\bar{C}$  with KI or NaI in acetone solns. gives CO +  $I_2$  (use in detn. of  $\bar{C}$  (91) (92) (93)).]

[The behavior of  $AlCl_3$  with  $\bar{C}$  has been extensively studied; for studies of solns. of  $AlCl_3$  in liq.  $\bar{C}$  from viewpoint of vapor pressure (268), density (269), and conductance (270) see indic. refs. — For general studies of liq.  $\bar{C}$  as solvent (271) (272) including studies on system  $\bar{C}$  +  $Cl_2$  (273) and on phosgeno salts such as calcium phosgeno-aluminate (274) (275) and others (276) see indic. refs.].

Behavior with various inorganic nitrogen compounds. With  $NH_3$ . [ $\bar{C}$  in lgr. (277) or  $C_6H_6$  (278) gives urea, biuret, cyanuric acid, cyamelide, ammelide, etc.;  $\bar{C}$  as gas with  $NH_3$  as gas gives urea (279) cf. (280) (143), guanidine, cyanuric acid (281), and cyamelide (282). — For reaction of  $\bar{C}$  in toluene soln. with aq.  $NH_4OH$  as a source of isocyanic acid see (283). — Note also that  $\bar{C}$  with sodamide reacts in cold in sense  $COCl_2 + 3NaNH_2 \rightarrow NaNCO + 2NaCl + 2NH_3$ , but at about 250° in sense  $COCl_2 + 5NaNH_2 \rightarrow Na_2N-C\equiv N + 2NaCl + NaOH + 3NH_3$  (284).]

[ $\bar{C}$  with  $NH_4Cl$  at elevated temps., e.g., 200–400°, gives (285) (286) carbamyl chloride,  $NH_2.CO.Cl$  [Beil. III-31, III<sub>1</sub>-(15)], b.p. 61–62° dec. (285). — For study of analogous carbamyl fluoride and carbamyl bromide (previously unknown) see (287).]

With hydroxylamine. [For studies on behavior of  $\bar{C}$  with  $NH_2OH$  see (288) (289)]

With hydrazine: [ $\bar{C}$  with 1 mole hydrazine would be expected to give *N*-aminocarbamyl chloride,  $NH_2.NH.CO.Cl$ , but this compound appears to be unknown;  $\bar{C}$  with 2 moles hydrazine should yield *N,N'*-diaminourea (carbohydrazide) [Beil. III-121, III<sub>1</sub>-(57), III<sub>2</sub>-(96)], but this compound has not been reported as prepd. by this method.]

#### BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

With hydrocarbons. [For studies on photochem. reaction of  $\bar{C}$  with alkanes (290) or with cycloalkanes (291) or with aliphatic or alicyclic acid chlorides (292) as a means of replacement of hydrocarbon H atoms by the  $CO.Cl$  group see indic. refs. — For reaction of  $\bar{C}$  with satd. nonaromatic hydrocarbons in pres. of cat. yielding ketones see (293). — Note also that  $\bar{C}$  with  $CH_4 + H_2 + cat.$  is claimed (236) to give acetaldehyde (1:0100).]

$\bar{C}$  with aromatic hydrocarbons in pres. of a Friedel-Crafts' type cat. condenses according to conditions with either one or two moles of hydrocarbon yielding, respectively, the corresp. acid chloride or ketone. No attempt can be made here to collect the reported cases of these types since the many acid chlorides contained in this book afford numerous examples.

[ $\bar{C}$  with ethylene +  $AlCl_3$  in  $CS_2$  adds to the unsatd. linkage giving (295) (296) (297) (298)  $\beta$ -chloropropionyl chloride (3:5690) although the method has been questioned (299) (300). —  $\bar{C}$  with propylene +  $AlCl_3$  as directed (301) gives  $\beta$ -chloroisobutyryl chloride (3:9101).] [ $\bar{C}$  with acetylene (302) or acetylene homologs (303) gives complex condensation products suitable for molding.]

With alcohols.  $\bar{C}$  with alcohols reacts according to circumstances with either 1 mole alcohol giving the corresponding chloroformate (chlorocarbonate) esters, or with 2 moles alcohol giving the corresponding carbonate ester. The countless known cases cannot here be cited in detail but the following examples are given; see also the summary of Dyson (308).

$\bar{C}$  with MeOH (1:6120) gives (304) methyl chloroformate (3:5075) q.v. and/or dimethyl carbonate (1:3046);  $\bar{C}$  with EtOH (1:6130) gives ethyl chloroformate (3:7295) q.v. and/or diethyl carbonate (1:3150);  $\bar{C}$  with *n*-PrOH (1:6150) gives *n*-propyl chloroformate (3:7540) q.v. and/or di-*n*-propyl carbonate (1:3373);  $\bar{C}$  with isopropyl alcohol (1:6135) gives isopropyl chloroformate (3:7405) q.v. and/or di-isopropyl carbonate (1:3261);  $\bar{C}$  with *n*-butyl alcohol (1:6180) gives *n*-butyl chloroformate (3:7980) q.v. and/or di-*n*-butyl carbonate (1:3626);  $\bar{C}$  with isobutyl alcohol (1:6165) gives isobutyl chloroformate (3:7760) q.v. and/or di-isobutyl carbonate (1:3501);  $\bar{C}$  with *n*-AmOH (1:6205) presumably gives *n*-amyl chloroformate (3:9380) q.v., but di-*n*-amyl carbonate appears to be unreported;  $\bar{C}$  with isoamyl alcohol (1:6200) gives isoamyl chloroformate (3:8215) q.v. and/or di-isoamyl carbonate (1:3937).

$\bar{C}$  with allyl alcohol (1:6145) gives allyl chloroformate (3:7487) q.v. and/or diallyl carbonate;  $\bar{C}$  with cyclohexanol (1:6415) gives cyclohexyl chloroformate (3:5770) q.v.;  $\bar{C}$  with benzyl alcohol (1:6480) gives benzyl chloroformate (3:9565) q.v. — [For analogous reaction of  $\bar{C}$  with unsatd. monohydric alcohols such as methallyl alcohol, crotyl alcohol, etc., see (305).]

$\bar{C}$  with monohydroxyethers gives analogous products: e.g.,  $\bar{C}$  with  $\beta$ -methoxyethanol (1:6405) gives  $\beta$ -methoxyethyl chloroformate (3:9140) q.v.;  $\bar{C}$  with  $\beta$ -ethoxyethanol (1:6410) gives  $\beta$ -ethoxyethyl chloroformate (3:9250) q.v. — [For reaction of  $\bar{C}$  with polyhydroxyethers such as diethylene glycol (1:6525), triethylene glycol (1:6538), tetraethylene glycol, etc., giving corresp. bis-(chloroformates), see (306).]

[For study of behavior of  $\bar{C}$  toward various alkali alkoxides see (307).]

[Note that  $\bar{C}$  as liq. reacts with enol form of acetone (1:5900) in  $\frac{1}{2}$  hr. at room temp. giving (330) isopropenyl chloroformate (3:7358).]

With phenols. The reaction of  $\bar{C}$  with phenols is more sluggish than with alcohols, and the corresp. diaryl carbonates are usually obtained from  $\bar{C}$  with 2 moles of the corresponding sodium phenolate cf. (308).

[ $\bar{C}$  (as liquid) with phenol (1:1420) in s.t. at 140–150° (309), or  $\bar{C}$  in toluene (310) or trichloroethylene (3:5170) (311) with aq. phenol (311) or aq. Na phenolate (310), or  $\bar{C}$  with Na phenolate in toluene (312), or  $\bar{C}$  with 10% aq. Na phenolate at 30° (313) gives (yields: 45% (312), 44% (313)) phenyl chloroformate [Beil. VI-159, VI<sub>1</sub>-(88), VI<sub>2</sub>-(157)], b.p. 97–98° at 25 mm. (310), 83–84° at 12 mm. (313),  $n_D^{25} = 1.5180$  (313); for use as acylating agent see (314).]

[ $\bar{C}$  in toluene shaken with a soln. of *o*-cresol (1:1400) in aq. NaOH (310) (315) gives *o*-tolyl chloroformate [Beil. VI-356], b.p. 119° at 35 mm. (310), 114° at 25 mm. (310). —  $\bar{C}$  in toluene shaken with a soln. of *m*-cresol (1:1730) in aq. NaOH (315) gives *m*-tolyl chloroformate [Beil. VI-379], b.p. 103° at 22 mm. (315). —  $\bar{C}$  in toluene shaken with a soln. of *p*-cresol (1:1410) in aq. NaOH (315), or  $\bar{C}$  passed as gas into aq. Na *p*-cresolate below 10° (316), gives (78–80% yield (316)) *p*-tolyl chloroformate [Beil. VI-393, VI<sub>2</sub>-(380)], b.p. 108° at 30 mm. (315) (316).]

Countless other phenols behave with  $\bar{C}$  in generally similar fashion but cannot be detailed here.

With carboxylic and sulfonic acids.  $\bar{C}$  with carboxylic acids or sulfonic acids or their salts at elevated temps. or in pres. of tertiary bases effects conversion to the corresponding carboxylic acid chlorides or sulfonyl chlorides.

[E.g.,  $\bar{C}$  with AcOH (1:1010) at 110–120° (317), or at 160° over  $MgCl_2$  on diatomaceous earth (318) cf. (319) (320), or  $\bar{C}$  with NaOAc at 120° under press. (321), or  $\bar{C}$  with  $Ac_2O$  (1:1015) + cat. (322) gives acetyl chloride (3:7065). —  $\bar{C}$  with chloroacetic acid (3:1370) over activated carbon at 200° gives (323) chloroacetyl chloride (3:5235). —  $\bar{C}$  with anhydrous oxalic acid (1:0535) in pres. of tertiary amines yields (324) oxalyl (di)chloride

(3:5060). —  $\bar{C}$  with cinnamic acid (1:0735) in pres. of tertiary amines yields (324) cinnamoyl chloride (3:0330). —  $\bar{C}$  with phenoxyacetic acid (1:0680) in pres. of tertiary amines yields (324) phenoxyacetyl chloride (3:8790). —  $\bar{C}$  with lauric acid (1:0605) at 140–150° gives (85–90% yield (325)) lauroyl chloride (3:9858). —  $\bar{C}$  with palmitic acid (1:0650) at 140–150° gives (70–75% yield (325)) palmitoyl chloride (3:9912). —  $\bar{C}$  with stearic acid (1:0660) at 140–150° gives (70–75% yield (325)) stearoyl chloride (3:9960). —  $\bar{C}$  with oleic acid (1:0565) gives (325) oleoyl chloride (3:9940).]

[ $\bar{C}$  with benzoic acid (1:0715) at 140–200° (326), or in pres. of tertiary bases or their salts (324), or  $\bar{C}$  with  $\text{AgOBz}$  in s.t. at 100° (327) gives benzoyl chloride (3:6240). —  $\bar{C}$  with salicylic acid (1:0780) in toluene (328) or in  $\text{C}_6\text{H}_6$  in presence of tertiary bases (324) gives salicyloyl chloride (3:0085). —  $\bar{C}$  with furoic acid (1:0475) under press. at not above 100° gives (329) furoyl chloride (3:8515).]

[Many other cases including sulfonic acids, e.g., (324), cannot be detailed here.]

With amines. With primary amines.  $\bar{C}$  with primary amines reacts in various ways according to conditions to yield *N*-alkyl (or aryl) carbamyl chlorides, *N*-alkyl (or aryl) isocyanates, or *N,N'*-dialkyl (or aryl) ureas. Examples of these types of reaction are included below.

[ $\bar{C}$  with  $\text{CH}_3\text{NH}_2\cdot\text{HCl}$  at 250–300° gives (285) (331) *N*-methylcarbamyl chloride [Beil. IV-64]; for stabilization of this prod. by formn. of insol. compds. with  $\text{AlCl}_3$ , etc., see (332); note that treatment with  $\text{CaO}$  causes loss of  $\text{HCl}$  giving (285) methyl isocyanate [Beil. IV-77, IV<sub>1</sub>-(337), IV<sub>2</sub>-(578)], best prepd. by other means, e.g., from  $\text{NaN}_3$  with  $\text{Ac}_2\text{O}$  (333) or  $\text{AcCl}$  (334) (335). —  $\bar{C}$  with  $\text{CH}_3\text{NH}_2$  in  $\text{C}_6\text{H}_6$  + aq. alkali, however, gives *N,N'*-dimethylurea [Beil. IV-65, IV<sub>1</sub>-(331), IV<sub>2</sub>-(568)], m.p. 106°.]

[ $\bar{C}$  with  $\text{C}_2\text{H}_5\text{NH}_2\cdot\text{HCl}$  at 250–300° gives (285) *N*-ethylcarbamyl chloride [Beil. IV-114]; note that treatment of this prod. with  $\text{CaO}$  causes loss of  $\text{HCl}$  giving (285) ethyl isocyanate [Beil. IV-122, IV<sub>1</sub>-(357), IV<sub>2</sub>-(613)], b.p. 60°.]

[ $\bar{C}$  with other primary aliphatic or cycloaliphatic amine hydrochlorides under conditions such that  $\text{HCl}$  is removed from reaction mixt. gives corresp. isocyanates (336) cf. (337).]

[ $\bar{C}$  with aniline hydrochloride presumably yields *N*-phenylcarbamyl chloride [Beil. XII-346, XII<sub>1</sub>-(230)], m.p. 53–59°, but this compound is usually prepd. by other means (338) (339) since it readily loses  $\text{HCl}$  at 90–100° or by action of aq. or aq. alk. (340) giving phenyl isocyanate; for stabilization of *N*-phenylcarbamyl chloride by formn. of molecular compound with  $\text{AlCl}_3$  see (332). —  $\bar{C}$  in dry aniline (341) or aq. aniline (342) (96) gives *N,N'*-diphenylurea (carbanilide) [Beil. XII-352, XII<sub>1</sub>-(233)], m.p. 238°; for use of this reaction as method of quant. detn. of  $\bar{C}$  see (94) (95) cf. (91). —  $\bar{C}$  with fused aniline  $\text{HCl}$  or carbanilide (343), or  $\bar{C}$  with aniline  $\text{HCl}$  in  $\text{C}_6\text{H}_6$  at 120° under press. (344) cf. (337), gives phenyl isocyanate [Beil. XII-437, XII<sub>1</sub>-(259)], b.p. 166°.]

$\bar{C}$  with countless other arom. prim. amines behaves in generally similar fashion but details cannot be included here [however, for reaction of  $\bar{C}$  with *p*-nitroaniline in  $\text{EtOAc}$  soln. giving *N*-*p*-nitrophenylcarbamyl chloride which on recrystn. from  $\text{CCl}_4$  loses  $\text{HCl}$  yielding *p*-nitrophenyl isocyanate see (345) (346) (347)].

With secondary amines. [ $\bar{C}$  with  $(\text{CH}_3)_2\text{NH}$  in  $\text{C}_6\text{H}_6$  at 0° (348) (349), or  $\bar{C}$  over fused  $(\text{CH}_3)_2\text{NH HCl}$  (350) (351), gives *N,N'*-dimethylcarbamyl chloride [Beil. IV-73], h.p. 167°, which with dimethylamine in  $\text{C}_6\text{H}_6$  yields (349) *N,N,N',N'*-tetramethylurea [Beil. IV-74, IV<sub>1</sub>-(335), IV<sub>2</sub>-(574)], liquid, b.p. 177°.]

[ $\bar{C}$  with  $(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HCl}$  at elev. temp. (350), or with  $(\text{C}_2\text{H}_5)_2\text{NH}$  in  $\text{C}_6\text{H}_6$  (352), gives *N,N*-diethylcarbamyl chloride [Beil. IV-120, IV<sub>2</sub>-(611)], liquid, h.p. 186–190°, which with diethylamine gives (353) cf. (354) *N,N,N',N'*-tetraethylurea [Beil. IV-120, IV<sub>2</sub>-(611)], liquid, b.p. 210–215°.]

[ $\bar{C}$  with piperidine  $\text{HCl}$  would be expected to give *N*-piperidylformyl chloride ("penta-

methylenecarbamyl chloride") [Beil. XX-54], b.p. 237-238°, but this compound has been reported only by other means.]

$\bar{C}$  with aromatic secondary amines behaves in generally analogous fashion but cannot be detailed here.

*With tertiary amines.* [ $\bar{C}$  with *N,N*-dimethylaniline at ord. temp. is claimed (355) (356) to give 4,4'-bis-(dimethylamino)benzophenone ("Miehler's ketone") [Beil. XIV-89; XIV-1-(391)], m.p. 174°. However,  $\bar{C}$  passed into boiling *N,N*-dimethylaniline evolves  $\text{CH}_3\text{Cl}$  (3.7005) and gives (almost quant. yield (357)) *N,N'*-dimethyl-*N,N'*-diphenylurea [Beil. XII-418, XII-1-(251)], m.p. 121°. — Similarly,  $\bar{C}$  with boiling *N,N*-diethylaniline evolves  $\text{C}_2\text{H}_5\text{Cl}$  (3.7015) and gives *N,N'*-diethyl-*N,N'*-diphenylurea [Beil. XII-422], m.p. 79°]

[For use of  $\bar{C}$  in sepn. of a mixture of aniline, *N*-ethylaniline, and *N,N*-diethylaniline see (361).]

*With arylhydrazines* [ $\bar{C}$  in toluene added to cold ether soln. of phenylhydrazine gives (358) 1,5-diphenylcarbohydrazide ("diphenylcarbazine") [Beil. XV-292, XV-1-(72)], m.p. 175-175.5° u.c. when pure (359) For use of this reaction, followed by  $\text{CuSO}_4$  treatment of the resultant product, as a delicate test for  $\bar{C}$  see (78).]

*With other nitrogenous organic reactants* [For a concise review of behavior of  $\bar{C}$  with other nitrogenous classes such as amides, amidoximes, thioureas, thiosemicarbazides, etc., see the review of Dyson (360).]

*With hexamethylenetetramine.*  $\bar{C}$  with hexamethylenetetramine in  $\text{CHCl}_3$  gives (362) (363) (364) a compound of compn.  $\bar{C} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ , m.p. 187-190° dec., (363) 196-197° from  $\text{MeOH}$  (364). — [For use of hexamethylenetetramine in paints protective against  $\bar{C}$  see (365); for use of alumina or silica gels contg. hexamethylenetetramine as absorbents for  $\bar{C}$  see (366).]

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3:5005 1,1-DICHLOROETHYLENE  $\text{H}_2\text{C}=\text{C}-\text{Cl}$   $\text{C}_2\text{H}_2\text{Cl}_2$  Beil. I - 186  
(Vinylidene (di)chloride;  $\text{Cl}$  I<sub>1</sub>-(77)  
*unsym.*-dichloroethylene) I<sub>2</sub>-(158)

B.P. 31.7° at 760 mm. (1) F.P. -122.1° (1)  $D_4^{20} = 1.2129$  (1)  $n_D^{20} = 1.4249$  (1)

Care must be taken to avoid confusion of  $\bar{\text{C}}$  with vinyl chloride (3:7010), with 1,2-dichloroethane (ethylene (di)chloride) (3:5130), or especially with the isomeric compounds *cis*-1,2-dichloroethylene (3:5042), *trans*-1,2-dichloroethylene (3:5028), or their ordinary mixture (3:5030).

$\bar{\text{C}}$  when pure is colorless liq. with mild and characteristic odor; note, however, that at temps. above 0° and especially in pres. of oxygen or other cat.  $\bar{\text{C}}$  polymerizes to a white powder insoluble in the monomeric  $\bar{\text{C}}$ . (For much further comment on polymerization see below.)

#### PREPARATION OF $\bar{\text{C}}$

[For prepn. of  $\bar{\text{C}}$  from 1,1,2-trichloroethane (3:5330) by elimination of 1 HCl with alc. KOH (2) (by this process  $\bar{\text{C}}$  was initially prepared (3)), or with excess aq.  $\text{Ca}(\text{OH})_2$  at 70-80° (90% yield (4)) (5), or with aq. or alc.  $\text{NH}_3$  at ord. temp. (100% yield (7)), or with Na in dry ether (36) see indic. refs.; from 1,1,1-trichloroethane (3:5085) with excess aq.  $\text{Ca}(\text{OH})_2$  at 70-80° see (4) (5); for formn. of  $\bar{\text{C}}$  (as by-product of the isomeric 1,2-dichloroethylenes (3:5030)) from trichloroethane by catalytic pyrolytic dehydrochlorination see (6).]

[For prepn. of  $\bar{\text{C}}$  from 1,1,1,2-tetrachloroethane (3:5555) by loss of HCl by actn. of aq. + Fe, Zn, or Cd on warming under reflux see (8); from 1-bromo-1,1,2-trichloroethane by loss of Br-Cl with Zn dust + boilg. alc. see (37).]

[For formn. of  $\bar{\text{C}}$  (together with vinyl chloride) from ethyl trichloroacetate (3:5950) by actn. of Zn in alc. see (9).]

[For formn. of  $\bar{\text{C}}$  (20% yield) from 1,2-dichloroethane (ethylene (di)chloride (3:5130) with  $\text{Cl}_2$  in pres. of  $\text{AlCl}_3/\text{NaCl}/\text{FeCl}_3$  at 400-480° see (10); note that some 22% 1,2-dichloroethylenes (3:5030) + 29% trichloroethylene (3:5170) + 29% higher chlorination prods. are also formed.].

#### PURIFICATION AND STABILIZATION OF MONOMERIC $\bar{\text{C}}$

[For purification of  $\bar{\text{C}}$  by distn. as an azeotrope with MeOH, followed by removal of the latter by extraction with aq., see (11).]

Many compds. recommended as stabilizers or polymerization inhibitors for monomeric  $\bar{C}$  have been described in patents: e.g., see (12) (13) (14) (15) (16).

### CHEMICAL BEHAVIOR OF MONOMERIC $\bar{C}$

$\bar{C}$  + chlorine. [ $\bar{C}$  with  $Cl_2$  at 25–35° in pres. of absence of cat. adds 1 mole halogen giving (85–92% yield (17)) 1,1,1,2-tetrachloroethane (3:5555).]

$\bar{C}$  + bromine.  $\bar{C}$  with  $Br_2$  adds 1 mole halogen yielding (18) 1,1-dichloro-1,2-dibromoethane [Beil. I-93], oil, b.p. 175° at 760 mm. decg., 65° at 13 mm., f.p. –66.85°,  $D_4^{25} = 2.2203$ ,  $D_4^{20} = 2.2449$ ,  $D_4^{15} = 2.2695$ ,  $n_D^{25} = 1.55930$  (18).

$\bar{C}$  + hydrogen chloride.  $\bar{C}$  with dry  $HCl$  gas at 25–35° in pres. of  $AlCl_3$  or  $FeCl_3$  adds 1 mole  $HCl$  giving (85–90% yields (19) (20)) 1,1,1-trichloroethane (3:5085).

$\bar{C}$  + hydrogen bromide. The addition to  $\bar{C}$  of  $HBr$  appears to be unreported.

Polymerization of  $\bar{C}$ . Polymerization of  $\bar{C}$  either with itself or with other cpds. (especially other substituted ethylene derivs.) leads to a large group of industrially important materials broadly designated as "vinylidene polymers." Certain plasticized and stabilized copolymer compositions have been named "Saran." [For extremely valuable comprehensive reviews of this general field see (1) (21) (22); in view of the comprehensive surveys and prior literature (including patents) references given (especially in (1)), the following text will in general include only citations since 1942.]

$\bar{C}$  when carefully purified and free from oxygen polymerizes only very slowly; however, in the pres. of various catalysts, notably peroxides, polymerization readily occurs (for amplification see (1)).

[For patents involving polymeric  $\bar{C}$  from viewpoint of purification (23), storage of super-cooled material (24), heat treatment to increase tensile strength (25), improvement of stability to light and heat (26) (27) (28) (29), or coloring (30) see indic. refs. — For studies on structure of fibers of polymeric  $\bar{C}$  see (1) (31). — For identification of common comml. plastics (including "Saran" and "Velon") see (32).]

[For review of copolymerization of  $\bar{C}$  see (1); for copolymerization with butadiene (33), with vinyl chloride or vinyl acetate (34), with styrene, acrylonitrile, various methacrylates, etc. (35), see indic. refs.]

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(11) Taylor, Horsle

(12) The Distillers C

(13) Coleman, Zemb

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Nov. 8, 1938; *Cent.* 1

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3:5010 DICHLOROACETYLENE  
(1,2-Dichloroethyne)



Beil I - 245

I<sub>1</sub>-(106)

I<sub>2</sub>-(222)

B.P.

F.P.

32-33° at 748 mm. (1) (2) (3)

-66 to -64.2° (1)

$D_4^{20} = 1.261$  (9)

29° cor. at 743 mm. (4)

$n_D^{20} = 1.42790$  (9)

Colorless oil which ignites in air and explodes even on stirring; however, its 5-10% soln. in ether is safely handled (4).

[For prepn. of  $\bar{C}$  from acetylene + aq. alk. KOCl soln. under  $N_2$  see (1) (2) (3); from 1,1,2-trichloroethylene (3:5170) in  $N_2$  at 130° over solid granular KOH (65% yield (4)) see (4) (5) (9); from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) with KOH in xylene under  $N_2$  (can be carried out as a lect. expt.) see (6) (9); for formn. of  $\bar{C}$  from barium salt of  $\alpha,\beta,\beta$ -trichloroacrylic acid (3:1840) by hgt. in  $H_2$  see (13).]

$\bar{C}$  forms with diethyl ether a molecular cpd.,  $\bar{C} \cdot \bar{C}_2H_5O$ , eas. decomposed by aq. into its components (5); for  $D$  and  $n$  of ether solns. of  $\bar{C}$  see (9).

$\bar{C}$  on combustion yields  $CO$ ,  $CO_2$ ,  $COCl_2$  (4) together with other products (5).

[For use of  $\bar{C}$  in extraction of coffee see (7).]

$\bar{C}$  in  $CCl_4$  treated 9 hrs. with strong  $Cl_2/CCl_4$  soln. gives (1) on evapn. hexachloroethane (3:4835), m.p. 187° in s.t. (1).

$\bar{C}$  on passing into  $Br_2/aq.$  yields (1) a heavy oil which on stdg. under the excess reagt. solidifies to cryst. of 1,2-dichloro-1,1,2,2-dibromoethane; after recrystn. from alc., m.p. 209-210° dec., with yellowing at 200° (1). [Note that  $\bar{C}$  in  $CCl_4$  treated with  $Br_2/CCl_4$  can add 1 mole  $Br_2$  giving (65% yield (4)) 1,2-dichloro-1,2-dibromoethylene, b.p. 172° at 760 mm. (8),  $D_4^{15} = 2.3036$  (8),  $n_D^{15} = 1.57954$  (8), m.p. +4.40° (8), 4.9° (4).]

$\bar{C}$  with  $I_2$  in ether (4) or  $CCl_4$  (5) gives slowly 1,2-dichloro-1,2-diiodoethylene, cryst. from ether or pet. eth., m.p. 70° (4). [Another stereoisomer, m.p. 5-7°, is formed only to extent of 10% and is removed by the solvent (5).]

[For studies on behavior of  $\bar{C}$  on polymerization (10), and its reactions with  $NH_3$  (10), amines (10) (11), alcoholates (10), diethyl sodio-malonate (10), organic Mg compds. (12), ethyl diazoacetate (12), and  $NO_2$  (12) see indic. refs.]

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### BINARY SYSTEMS CONTAINING $\bar{C}$ (See also azeotropes containing $\bar{C}$ )

$\bar{C} + Cl_2$ : for f.p./compn. data and diagram (various compounds and eutectics are formed) see (21).

$\bar{C} + C_2H_5Cl$  (3:7015): for f.p./compn. data and diag (eutectic, f.p.  $-149.7^\circ$ , conts. 31.7 wt. %  $\bar{C}$ ) see (17). —  $\bar{C} + CHCl_3$  (3:5050): for f.p./compn. data and diag. (eutectic, f.p.  $-103.4^\circ$ , conts. 70.5 wt. %  $\bar{C}$ ) see (17); for data on b.p.,  $D_4^{20}$ , and liq./vapor equilibria see (34). —  $\bar{C} + CCl_4$  (3:5100): for data on b.p.,  $D_4^{20}$ , and liq./vapor equilibria see (34). —  $\bar{C} + 1,1$ -dichloroethane (3:5035): for f.p./compn. data see (19). —  $\bar{C} + 2,2$ -dichloropropane (3:7140): for f.p./compn. data see (22).

$\bar{C} + isobutyl\ bromide$ : for f.p./compn. data see (19). —  $\bar{C} + methylene\ (di)bromide$ : for f.p./compn. data see (19).

$\bar{C} + methylene\ (di)iodide$ : for f.p./compn. data see (19).

$\bar{C} + dimethylaniline$ : for  $D_4^{25}$  and  $n_D^{24.5}$  for 0-100%  $\bar{C}$  see (23); for f.p./compn. data and diagram (eutectic, m.p.  $-97.2^\circ$ , conts. 91 wt. %  $\bar{C}$ ) see (168).

### TERNARY SYSTEMS CONTAINING $\bar{C}$ (See also azeotropes containing $\bar{C}$ )

$\bar{C} + CHCl_3 + CCl_4$ : system forms ternary eutectic, f.p.  $-111.4^\circ$ , contg. 60 wt. %  $\bar{C} + 27.0$  wt. %  $CHCl_3$  (3:5050) + 13.0 wt. %  $CCl_4$  (3:5100) (17).

### BINARY AZEOTROPES CONTAINING $\bar{C}$

$\bar{C} + H_2O$ :  $\bar{C}$  forms with aq. a const.-boilg. mixt., b.p.  $38.1^\circ$ , contg. 98.5 wt. %  $\bar{C}$  (68).  
 $\bar{C} + MeOH$ :  $\bar{C}$  forms with MeOH (1:6120) a const.-boilg. mixt., b.p.  $39.2^\circ$  (4) at 760 mm (3), contg. 92 wt. % (3), 94 wt. % (4)  $\bar{C}$ . —  $\bar{C} + EtOH$ :  $\bar{C}$  forms with EtOH (1:6130) a const.-boilg. mixt., b.p.  $41.0^\circ$  at 760 mm. (3), contg. 96.5 wt. % (3)  $\bar{C}$ . —  $\bar{C}$  forms with formaldehyde dimethylacetal (1:0105) a const.-boilg. mixt., b.p.  $45.0^\circ$  (36), contg. (36) 41 wt. %  $\bar{C}$ , cf. (37). —  $\bar{C} + acetone$ : note that this system forms no azeotrope; note also that  $\bar{C}$  is the only known liquid which with MeOH (see above) gives a const.-boilg. mixt. boilg. lower than acetone and at the same time not forming a binary azeotrope with acetone (4).

### TERNARY AZEOTROPES CONTAINING $\bar{C}$

$\bar{C} + H_2O + EtOH$ : forms no ternary azeotrope (68).

$\bar{C} + MeOH + acetone$ : this system forms no ternary azeotrope; for discussion see (4) (38).

$\bar{C} + CHCl_3 + acetone$ : for discussion see (4).

### OTHER PHYSICAL PROPERTIES OF $\bar{C}$

[For study of thermal conductivity of  $\bar{C}$  see (39); for studies of heat capacity of  $\bar{C}$  (40) as calculated from spectroscopic data (41) see indic. refs.; for studies of critical temp. of  $\bar{C}$  (7) (15) (6) and method for its microdetermination (6) see indic. refs.; for ebullioscopic const., viz.,  $2.6^\circ$  for 1000 g.  $\bar{C}$ , see (43).]

[For studies of adsorption of  $\bar{C}$  on wood charcoal at  $25^\circ$  and  $50^\circ$  (44) or on coconut charcoal over range  $-31.5^\circ$  to  $184^\circ$  (45), on  $Al(OH)_3$  gel (46), on  $Fe(OH)_3$  gel (47), on  $Cr_2O_3$  (48) see indic. refs.;  $\bar{C}$  is preferentially adsorbed (42) by silica gel from its mixt. with  $CHCl_3$  (3:5050).]

[For study of attempt to separate isotopes of  $Cl_2$  by reversible fractional distn. of  $\bar{C}$  see (49).]

PHYSIOLOGICAL ASPECTS OF  $\bar{C}$ 

$\bar{C}$  has low toxicity compared to other chlorinated hydrocarbon solvents; the maximum allowable conc. for 8 hrs. daily exposure is 500 p p m. (50). [For study of relative toxicity of  $\bar{C}$  see (51); for extensive study of industrial hygiene and toxicity of  $\bar{C}$  (together with 12 other chlorinated solvents (52)) (53) (50) see indic. refs.; for study of  $\bar{C}$  upon running activity of male rat see (54).]

USES OF  $\bar{C}$ 

$\bar{C}$  is widely used as a solvent, as a fluid for refrigeration processes, and for removing water from other organic materials; examples of all these aspects are cited below.

[For study of utility of  $\bar{C}$  as solvent for the ozonization of org. compds. see (10); for use of  $\bar{C}$  as solvent for the extraction of vitamin A (55) or of soy-bean oil (56) see indic. refs.; for general studies (15) (57) (58) and patents (59) (60) (61) (62) (63) (64) (65) on use of  $\bar{C}$  in refrigerating machines and systems see indic. refs.; for use of  $\bar{C}$  in detn. of water content of liquids (66) (67) or for prepn. of abs. EtOH (68) (69) (70) see indic. refs.]

DETECTION OR DETERMINATION OF  $\bar{C}$ 

[For detection of  $\bar{C}$  in pres. of acetone (by means of Fujiwara color test with pyridine + NaOH) see (71); for distinction of  $\bar{C}$  from  $\text{CHCl}_3$  (3:5050) and from  $\text{CCl}_4$  (3:5100) by color tests see (72) (73) (also under  $\bar{C}$  below).]

[For detn. of  $\bar{C}$  in blood by removal through aeration, pyrolytic decompn. of  $\bar{C}$ , and alk. absorption of resultant HCl as directed see (74); for detn. of C, H, and Cl in  $\bar{C}$  by combustion see (75). Note that the R. + H. Tri-Per Analyzer, a recording ultra-violet photometer very useful for detn. of trichloroethylene (3:5170) and tetrachloroethylene (3:5460), is insensitive (76) to  $\bar{C}$ .]

PREPARATION OR FORMATION OF  $\bar{C}$ 

From methane. [The chlorination of  $\text{CH}_4$  under various conditions to yield  $\bar{C}$  (accompanied by more or less  $\text{CH}_3\text{Cl}$  (3:7005),  $\text{CHCl}_3$  (3:5050), and  $\text{CCl}_4$  (3:5100)) has been extensively studied and no attempt will be made here to sift out details. For examples of leading scientific papers ((77)-(88), incl.) and patents ((89)-(96), incl.) see indic. refs.]

From methyl chloride. [The chlorination of  $\text{MeCl}$  to  $\bar{C}$  has also been extensively studied; many of the relevant data are included in the papers and patents on the chlorination of methane (see preceding paragraph), to which should be added the following patents (91) (97) (98) (99) (100). Note patent (98) on separation of  $\text{MeCl}$  (3:7005) from  $\bar{C}$  by hydrolysis of former to  $\text{MeOH}$  (1:6120) with  $\text{Ca}(\text{OH})_2$  under press.]

From chloroform. [For formn. of  $\bar{C}$  from  $\text{CHCl}_3$  (3:5050) by replacement of 1 chlorine by hydrogen using  $\text{Zn} + \text{alc. HCl}$  (101),  $\text{Zn} + \text{AcOH}$  (103),  $\text{Zn}$  dust + alc.  $\text{NH}_3$  (102) (8) (2),  $\text{Al/Hg} + \text{aq.}$  (103),  $\text{Fe} + \text{AcOH}$  (103), or  $\text{Si}_2\text{H}_5 + \text{AlCl}_3$  in absence of air (104) see indic. refs.]

From carbon tetrachloride. [For prepn. of  $\bar{C}$  from  $\text{CCl}_4$  (3:5100) using aq.  $\text{FeSO}_4 + \text{NaOH}$  see (105).]

From miscellaneous sources. [For prepn. or formn. of  $\bar{C}$  from  $\text{CH}_2\text{I}_2$  with  $\text{Cl}_2$  (first prepn. of  $\bar{C}$ ) (106) cf. (158); from polyoxymethylene with  $\text{PCl}_5$  in s t. (107); from  $\text{MeOH} + \text{S}_2\text{Cl}_2 + \text{Cl}_2$  (108); or from chloroacetic acid (3:1370) by electrochem. oxidn. (109) see indic. refs.]

CHEMICAL BEHAVIOR OF  $\bar{C}$ 

Oxidation of  $\bar{C}$ . [ $\bar{C}$  with air at ord. temps. and press. does not give inflammable mixts.; at high temps. vapor of  $\bar{C}$  becomes inflammable and ignites at  $642^\circ$  in air, at  $606^\circ$  in  $\text{O}_2$ ;

limiting condens. of  $\bar{C}$  for inflammability in  $O_2$  are 15.5–66.4%;  $N_2$  does not greatly affect the lower limit of inflammability in  $O_2$  but greatly reduces the upper limit (110). — For study of inflammability of mixts. of  $\bar{C}$  with  $O_2$  +  $N_2$ , air +  $CO$ , or  $O_2$  +  $N_2$  +  $MeBr$  see (111). — For effect of  $\bar{C}$  on flash point of solvents see (115).]

[ $\bar{C}$  with atomic  $O$  gives (112)  $COCl_2$  (3:5000),  $Cl_2$ ,  $HI$ ,  $CO_2$  +  $H_2O$ ;  $\bar{C}$  with air over  $CuO$  at  $450^\circ$  gives (113) little  $COCl_2$  (3:5000); for study of  $Cl_2$ -sensitized photochem. oxidn. of  $\bar{C}$  see (114).]

Fluorination of  $\bar{C}$ . [ $\bar{C}$  with  $SbF_5$  + cat. readily gives (126) (127)  $CH_2F_2$ , b.p.  $-51.6^\circ$ , +  $CH_2ClF$ , b.p.  $-9.0^\circ$ .]

Chlorination of  $\bar{C}$ . [ $\bar{C}$  with  $Cl_2$  as directed (116) (117), or  $\bar{C}$  with  $HI$  gas + air over  $CuCl_2$  at  $440^\circ$  (118), gives  $CHCl_3$  (3:6050) and  $CCl_4$  (3:5100).]

Bromination of  $\bar{C}$ . [ $\bar{C}$  with  $Br_2$  cf. (158) in pres. of  $Al$  gives (128) cf. (129)  $CH_2BrCl$  +  $CH_2Br_2$  (Boil. I-67, I<sub>1</sub>-(10), I<sub>2</sub>-(32)), b.p.  $96.95^\circ$  at 760 mm., f.p.  $-52.7^\circ$ ,  $D_4^{25} = 2.48417$ ,  $D_4^{20} = 2.49702$  (130). — For an alternative synthesis of  $CH_2Br_2$  (88–90% yield) from  $CH_2Br_2$  with  $Na_3AsO_4$  +  $NaOH$  see (138).]

Hydrolysis of  $\bar{C}$ .  $\bar{C}$  on suitable hydrolysis yields formaldehyde (1:0145). [E.g.,  $\bar{C}$  with aq. in pres. of weakly alk. reacting salts such as  $NaHCO_3$ ,  $Na_2HPO_4$ ,  $NaOAc$ , etc., at  $105^\circ$  under press. (119), or  $\bar{C}$  +  $N_2$  over dry  $Na_2CO_3$  at  $310$ – $320^\circ$  (120),  $\bar{C}$  with steam over activated carbon at  $260$ – $270^\circ$  (121),  $\bar{C}$  with aq. at  $140$ – $170^\circ$  under press. (122),  $\bar{C}$  with steam at  $550$ – $850^\circ$  over cat. (123), or  $\bar{C}$  with steam over tin phosphite at  $460^\circ$  (124) gives formaldehyde (1:0145) +  $HI$ . Note that  $\bar{C}$  on protracted htg. with aq. at  $180^\circ$  gives (125) formic acid (1:1005),  $MeCl$  (3:7005),  $MeOH$  (1:6120)  $HI$  +  $CO$ .]

Behavior with inorganic salts. [ $\bar{C}$  with  $NaI$  in acetone liqd. in press. bottle for 20 hrs. as directed (131), or  $\bar{C}$  with  $NaI$  in acetone,  $MeOH$ , or  $EtOH$  at  $120$ – $130^\circ$  under press. (132), gives (60% yield (131)) methylene (di)iodide [Boil. I-71, I<sub>1</sub>-(18), I<sub>2</sub>-(37)], b.p.  $151$ – $153^\circ$  cor. at 330 mm. (133),  $88^\circ$  at 39 mm. (134),  $66$ – $67^\circ$  at 11–12 mm. (24); exists in two crystn. forms, stable form, m.p.  $+5.85^\circ$  (135), metastable form, m.p.  $40^\circ$  (136);  $D_4^{25} = 3.2078$  (130);  $D_4^{20} = 3.3212$  (130);  $D_4^{16} = 3.3345$  (130);  $n_D^{25} = 1.74428$  (130). — For an alternative synthesis of  $CH_2I_2$  (90–97% yield) from iodoform by treatment with  $Na_3AsO_4$  +  $NaOH$  see (137).]

[ $\bar{C}$  with 2 moles  $K_2SO_5$  in aq. at  $150$ – $160^\circ$  gives potassium salt of methanedisulfonic acid (

[ $\bar{C}$  with alc.  $AgNO_3$  does not react even  $CHCl_3$  (3:5050) nor  $CCl_4$  (3:5100) reacts either,  $CH_2Cl$  (3:7005) gives a ppt. within 3 hrs. (140).]

[For formn. of polymeric prods. from reaction of  $\bar{C}$  with metal sulfides or polysulfides see (141); for study of photochem. reaction of  $\bar{C}$  with  $H_2S$  see (149).]

Behavior with metals.  $\bar{C}$  (like many other polyhalogenated hydrocarbons) in presence of metallic  $K$ ,  $Na$ ,  $K/Na$  alloy, or even of certain other active metals explodes under the influence of mechanical or thermal shock. [For study of this characteristic (142), especially with regard to sensitivity toward  $Li$ ,  $Na$ ,  $K$ ,  $Ca$ ,  $Sr$ ,  $Ba$  (143), see indie. refs.]

[Note that  $\bar{C}$  with molten sodium at  $260$ – $300^\circ$  gives (144)  $C$ ,  $H_2$ , and  $CH_4$ , together with smaller amts. of ethane, ethylene, and acetylene gives (145) 92%  $CH_4$  + 8% ethylene, while  $\bar{C}$  +  $Na$  vapor gives 92%  $CH_4$  + 8% ethylene; for further studies of behavior of  $\bar{C}$  attempts to obtain a free methylene radical ( $CH_2$ ) with  $\bar{C}$  +  $Na$  vapor have been unsuccessful (148).]

[For study of stability of various metals with respect to corrosion by  $\bar{C}$  under various conditions see (15).]

Behavior with various organic reactants.  $\check{C}$  with CO +  $AlCl_3$  at 260° and 800 atm. press. for 8 hrs. gives (150) chloroacetyl chloride (3:5235); but  $\check{C}$  with CO, COS, or  $COCl_2$  (3:5000) + cat. at 700° gives (151) malonyl (di)chloride (3:5030).]

$\check{C}$  with  $C_6H_6$  +  $AlCl_3$  gives (152) cf. (153) diphenylmethane (1:7120);  $\check{C}$  with toluene +  $AlCl_3$  gives (152) di-*p*-tolylmethane [Beil. V-615,  $V_1$ -(289),  $V_2$ -(518)], m.p. 28° (154), b.p. 302° cor. at 768 mm (154), accompanied by considerable (152) (155) 2,7-dimethylantracene, m.p. 241° cor. (153),  $\check{C}$  with *o*-xylene (1:7430) +  $AlCl_3$  in acetylene tetrachloride (3:5750) as solvent gives (156) 2,3,6,7-tetramethylantracene, m.p. 299° (156); for behavior of  $\check{C}$  in pres. of  $AlCl_3$  with *m*-xylene (1:7420) or with pseudocumene (1:7470) see (152).]

$\check{C}$  with  $CH_2Br_2$  + 5-10% KCl in pres. of moistened  $AlCl_3$  at 180° in s.t. for 16 hrs. undergoes a redistribution reaction giving (157) a mixt. contg 33%  $\check{C}$  + 18%  $CH_2Br_2$  + 50%  $ClCH_2Br$ ;  $\check{C}$  with  $CH_2I_2$  similarly treated at 114° for 18 hrs. gives (157) a mixt. contg. 33%  $\check{C}$  + 21%  $CH_2I_2$  + 46%  $ClCH_2I$ .]

$\check{C}$  with NaOMe in s.t. at 100° (158), or vapor of  $\check{C}$  over NaOMe + pumice at 200° (37), gives formaldehyde dimethylacetal (1:0105);  $\check{C}$  + NaOEt in s.t. at 100° (158), or  $\check{C}$  with excess EtOH + calcd amt. NaOH at 100-125° under press. (159), gives formaldehyde diethylacetal (1:0135); for analogous behavior of other alcoholates (158) (159) or phenolates (158) see indic. refs.]

$\check{C}$  with alc.  $NH_3$  at 125° in s.t. gives (160) hexamethylenetetramine [Beil. I-583,  $I_1$ -(306)]. —  $\check{C}$  with  $Me_2NH$  in s.t. at 70° gives (161) bis-(dimethylamino)methane. —  $\check{C}$  with  $Me_3N$  in 90% acetone at 55° or more slowly in ether undergoes a quaternization reaction giving trimethyl-chloromethyl-ammonium chloride (constants not detd.) (162).]

Ⓐ Beilstein test for halogen. Note that because of its low b.p.  $\check{C}$  often appears to fail in Beilstein copper gauze test for halogen compds.; in such cases use the modification described by (163) (164)

Ⓑ Hydrolysis to formaldehyde.  $\check{C}$  (2 g.) in 10% MeOH/alk. (20 ml.) boiled 20 min. under good reflux, subsequently acidified with dil.  $H_2SO_4$ , gives soln. containg.  $Cl^-$  and formaldehyde (1:0145).

Ⓒ Color reaction with  $\alpha$ -naphthol/cyclohexanol.  $\check{C}$  (1 drop) with 2 ml. of a 2% soln. of  $\alpha$ -naphthol (1:1500) in cyclohexanol (1:6415) + 1 pellet of solid NaOH, boiled 25 seconds and cooled, gives (72) blue color; one portion of this blue soln. underlaid with equal volume 85%  $H_2SO_4$ , stood 1 minute and shaken, turns green-blue; a second portion of the alkaline blue soln. acidified with equal volume of AcOH (1:1010) stood 1 minute and shaken becomes yellow. [Note that the alkaline boiling also gives a blue color with  $CHCl_3$  (3:5050) and with  $CCl_4$  (3:5100) while other chlorinated solvents (72) give yellow-brown, gray, or brown; in the  $H_2SO_4$  acidification both  $CHCl_3$  and  $CCl_4$  give blue rather than green-blue; in the AcOH acidification  $CHCl_3$  gives an orange-yellow,  $CCl_4$  a red color]

Ⓓ Color test with 2,7-dihydroxynaphthalene/cyclohexanol.  $\check{C}$  (1 drop) with 2 ml. pure cyclohexanol (1:6415) + 1 pellet NaOH + a few mgms. 2,7-dihydroxynaphthalene htd. at 197° (b.p. of ethylene glycol) for 45 seconds, decanted from undissolved NaOH, cooled, and shaken with 2 ml. AcOH + 4 ml. 96% EtOH, gives steel-blue color (73) [Note that under these conditions  $CHCl_3$  (3:5050) gives a deep-red color while  $CCl_4$  (3:5100) gives a pale yellow brown.]

Ⓔ Color test with cyclopentanol.  $\check{C}$  (1 drop) in cyclopentanol (1 ml.) with 1 pellet NaOH boiled 25 seconds, then shaken vigorously for 35 seconds, gives deep red color; upon addition of 4 ml. 96% EtOH and shaking color intensifies or becomes reddish brown (73). [Note that after addn. of alc.  $CHCl_3$  gives only a pale citron-yellow or

yellowish brown and that as little as 20% of  $\bar{C}$  can be detected by this means in  $CHCl_3$  (73);  $CCl_4$  gives (73) after addn. of alc. an intense nut-brown.]

— Formaldehyde di- $\alpha$ -naphthylacetal (methylene di- $\alpha$ -naphthyl ether): unreported.

⑩ Formaldehyde di- $\beta$ -naphthylacetal (methylene di- $\beta$ -naphthyl ether): m.p.  $134^\circ$  (165),  $133-134^\circ$  (166). [From  $CH_2I_2$  with Na  $\beta$ -naphtholate refluxed in alc. (165) (166) (167); not actually reported from  $\bar{C}$  but presumably resulting by above method if some KI be added to refluxing mixture of  $\bar{C}$  + Na  $\beta$ -naphtholate in acetone. Note that this ether fails (165) (167) to form any  $PKOH$  addition compound.]

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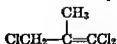
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3:5025 1,1,3-TRICHLORO-2-METHYLPROPENE-1  $C_4H_5Cl_3$ . Beil. S.N. 11



B.P. 45-46° (1)

Note:  $\bar{C}$  readily undergoes allyl transposition so that in reactions of  $\bar{C}$  products derived from the isomeric 1,1,1-trichloro-2-methylpropene-2 (3:5605) may be expected (1) (2) (3) [For prepn. of  $\bar{C}$  (57% yield (1)) from  $\beta,\beta,\beta$ -trichloro-*ter*-butyl alc. ("Chloretone") (3:2662) by hgt. to 200° with  $P_2O_5$  and dimethylaniline see (1).] [A 15% yield of the isomeric 1,1,1-trichloro-2-methylpropene-2 (3:5605) together with some  $\alpha$ -chloroisobutyric acid (3:0235) are separated from  $\bar{C}$  by redistillation (1).]

$\bar{C}$  on hydrolysis by boilg. 2 days with AgOH at 100° under pressure gives (22% yield (2)) 3,3-dichloro-2-methylpropen-2-ol-1, b.p. 78-79°,  $D_{20}^{20} = 1.298$ ,  $n_{20}^{20} = 1.493$ . [The corres. ether, b.p. 129° at 11 mm.,  $D_{20}^{20} = 1.330$ ,  $n_{20}^{20} = 1.5108$ , is also formed in 22%

yield (2). The alc. may be characterized by its *p*-nitrobenzoate, m.p. 91°, or its *N*-phenylcarbamate, m.p. 64° (2).

$\bar{C}$  on htg. with NaOAc + AcOH gives (2) 3,3-dichloro-2-methylpropen-2-yl acetate, b.p. 79° at 12 mm.,  $D_4^{20} = 1.257$ ,  $n_D^{20} = 1.4718$  (2). [With boilg. NaOH this ester regenerates the corresp. alc. (2).]

$\bar{C}$  with NaOH gives in the cold 70% yield (2) of 3,3-dichloro-2-methylpropen-2-yl ethyl ether, b.p. 56° at 12 mm.,  $D_4^{20} = 1.1285$ ,  $n_D^{20} = 1.4610$  (2).

$\bar{C}$  in  $\text{CHCl}_3$ , treated with  $\text{O}_3$ , then hydrolyzed gives  $\alpha$ -chloroacetone (3:5425), b.p. 60-62° at 50 mm. (1).

[For reactns. of  $\bar{C}$  with  $\text{CaI}_2$  and with  $\text{CH}_3\text{MgBr}$  see (2).]

④ 1,1,1,2,3-Pentachloro-2-methylpropane (3:1265): m.p. 59.5° (2). [From  $\bar{C}$  by direct treatment with  $\text{Cl}_2$  (2).]

⑤ 1,2-Dibromo-1,1,3-trichloro-2-methylpropane: m.p. 105° (2). [From  $\bar{C}$  on warming 1 day with excess  $\text{Br}_2$ , then distg. at 12 mm. (2).]

⑥ 3,3-Dichloro-2-methylpropen-2-yl *p*-nitrobenzoate: m.p. 91° (2). [From  $\bar{C}$  on boilg. with dil. alc. soln. of K *p*-nitrobenzoate (2).]

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3:5028 *trans*-1,2-DICHLOROETHYLENE  $\text{Cl}-\text{C}=\text{C}-\text{H}$   $\text{C}_2\text{H}_2\text{Cl}_2$  Bell. 1 —  
(*trans*-Acetylene dichloride)  $\text{H}-\text{C}=\text{C}-\text{Cl}$   $I_1$ -(78)  
 $I_2$ -(150)

B.P.		F.P.	
(18.8-50.2°	(35)]	-53.1° (34)	$D_4^{25} = 1.2480$ (1)
48.8°	at 763 mm. (1)	-53.0° (12)	$n_D^{25} = 1.43060$ (7)
48.1-49.4°	at 741 mm. (2)	-50.0° (13)	$D_4^{20} = 1.2560$ (1)
48.35°	at 760 mm. (3) (1) (13)		
48.3°	at 760 mm. (5)		$n_D^{15} = 1.11663$ (6)
48.2-48.4°	at 769 mm. (6)		
47.85-47.87°	at 769.5 mm. (7)		$D_4^{15} = 1.2651$ (3)
47.5°	(8)		1.2650 (1)
47.48°	(9)		$n_D^{15} = 1.41003$ (3)
47.3°	(10)		
47.2°	at 745 mm. (11)		
48.20-47.87°	at 769.5 mm. (27)		

See also both *cis*-1,2-dichloroethylene (3:5042) and ordinary (mixture of *cis* and *trans*) 1,2-dichloroethylene (3:5050); the following text is restricted to studies on substantially pure *trans* isomer.

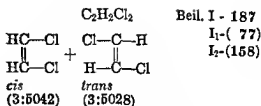
Note carefully that 1,2-dichloroethylene is not the same as ethylene (dichloride) (3:5130) (there are an almost incredible number of errors in the literature involving this point); neither is it the same as the now very important 1,1-dichloroethylene (vinylidene) (dichloride) (3:5041).

#### GENERAL DATA ON $\bar{C}$

Note that substantially pure  $\bar{C}$  is covered solvent in U.S.A. under designation "Dx 48" (referring to the two chlorine atoms and the h.p.l. [For study of thermal conductivity and for tabulation of constants of normal  $\bar{C}$  see (14) — For toxicity of  $\bar{C}$  see (26) (15) — For use of  $\bar{C}$  in extraction of caffeine from coffee see (16)]).



3:5030 1,2-DICHLOROETHYLENE } ord.  
(Acetylene dichloride) } mixt.



The text under this heading refers to the ordinary mixt. of the two individual stereoisomeric forms, viz., *cis*-1,2-dichloroethylene (3:5042) and *trans*-1,2-dichloroethylene (3:5028). Since the proportion of the two stereoisomers differs according to conditions and previous treatment no definite physical constants can be given, and those for each pure stereoisomer should be consulted.

Note carefully that 1,2-dichloroethylene is *not* the same as ethylene (di)chloride (3:5130) (there are an almost incredible number of errors in the literature involving this point); neither is it the same as 1,1-dichloroethylene (vinylidene (di)chloride) (3:5005).

Furthermore note that some confusion exists in the literature on the relationship between the two isomers; the high-boilg. stereoisomer (3:5042) is now definitely regarded as the *cis* form and the lower-boilg. stereoisomer (3:5028) as the *trans*; however, some records (including "International Critical Tables") have inverted these designations.

### PHYSICAL DATA ON $\bar{\text{C}}$

**General.** Ordinary comml.  $\bar{\text{C}}$  consists of a mixt. of the two stereoisomers; by careful fractional distn. the two stereoisomers can be separated (for references see text of the two pure stereoisomers). — An equilibrium mixt. contg. about 20% of the lower-boilg. (*trans*) (3:5028) and 80% of the higher-boilg. (*cis*) (3:5042) forms can be obt'd. from either by treatment at ord. temp. in sunlight with 1-2%  $\text{Br}_2$  (for data on thermal isomerization see text of both individual stereoisomers). — Note also that the two pure stereoisomers (q.v.) form a eutectic, f.p.  $-91^\circ$ , contg. about 29% *trans* + 71% *cis* forms.

**Solubility relationships of  $\bar{\text{C}}$ .** Soly. of  $\bar{\text{C}}$  in aq. is 0.8 ml. per 100 ml. aq. at ord. temp. (1). — [For soly. of  $\text{I}_2$  in  $\bar{\text{C}}$  over range  $11-25^\circ$  (2) and use of such solns. in detn.  $\text{I}_2$  number of oils and fats (3) (4) see indic. refs. — For solv. power of  $\bar{\text{C}}$  for various org. cpds. see (5) (6).]

**Inflammability of  $\bar{\text{C}}$ .**  $\bar{\text{C}}$  with air forms explosive mixt. in range contg. 3.3-15.3%  $\bar{\text{C}}$  (7); 9.7-12.8%  $\bar{\text{C}}$  (8). [For studies of influence of vapors of  $\bar{\text{C}}$  on mixts. of air with  $\text{CH}_4$  (8), acetylene (10), CO (10) (12), or  $\text{H}_2$  (10) see indic. refs.]

**Miscellaneous data.** [Ebullioscopic const. of  $\bar{\text{C}}$  (for 1 mole solute in 100 g.  $\bar{\text{C}}$ ) = 29.6 (14).]

### USES OF $\bar{\text{C}}$

[For use of  $\bar{\text{C}}$  as solv. for fats and oils (15), as refrigerating liquids (16) (17) (18) (19) (20) (21), for extraction of caffeine from coffee (22), for dehydration (concentration) of propionic acid from aq. solns. (23), for sepn. of *o*- and *p*-isomers of various phenols (24), in dewaxing of mineral lubricating oils (25), for pretreatment in dyeing of cellulose esters and ethers (26) see indic. refs.]

### PHYSIOLOGICAL BEHAVIOR OF $\bar{\text{C}}$

$\bar{\text{C}}$  acts as an anesthetic and narcotic, but full treatment of this aspect is beyond the scope of this work; for lead references, however, see below.

**Toxicity of  $\bar{\text{C}}$ .** [For studies on toxicity of  $\bar{\text{C}}$  see (27) (28) (29) (30) (31); for studies of narcotic action (31) (33) (34) (35) (36) see indic. refs.]

Antiseptic and disinfectant props. of  $\bar{C}$ . [For studies of  $\bar{C}$  from this viewpoint see (37) (38) (1).]

### DETERMINATION OF $\bar{C}$

$\bar{C}$  is detd. by conversion of its halogen by pyrolytic or by chem. means completely to chloride ion followed by either volumetric or gravimetric detn. of the latter.

[For detn. of  $\bar{C}$  by methods involving pyrolytic decompn. of  $\bar{C}$  see (39) (40) cf. (41).]

[For detn. of  $\bar{C}$  by methods involving decompn. of  $\bar{C}$  with Na + ethanolamine in dioxane see (42) cf. (43).]

[For detn. of  $\bar{C}$  by means of  $HgSO_4$  catalyzed addn. of  $Br_2$  (from bromide/bromate soln.) to its unsatd. linkage see (44).]

### PREPARATION OF $\bar{C}$

From various polychloroethanes. From 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). [For prepn. of  $\bar{C}$  from acetylene tetrachloride by removal of 2 chlorine atoms with  $H_2$  over Ni at 300–320° (45), with Fe or Al + aq. (46) (47) or Zn + aq. (47) (48), with acetylene over hydrogenating cat. (such as Ni) on activated carbon at 350° (49) preferably in pres. of aq. vapor (50), or by electrolytic reduction in pres. of  $ZnCl_2$  (51) cf. (52) see indic. refs. — Note that  $\bar{C}$  is also one of the prods. of pyrolysis of acetylene tetrachloride over pumice at 700° (53).]

From 1,1,1,2-tetrachloroethane (3:5555). [For prepn. of  $\bar{C}$  from unsym.-tetrachloroethane with acetylene over hydrogenating cat. (such as Ni) on activated carbon at 350° (49) preferably in pres. of aq. vapor (50) see indic. refs.; note that mechanism yielding this result is unknown.]

From 1,1,2-trichloroethane (3:5330). [For prepn. of  $\bar{C}$  from 1,1,2-trichloroethane (by loss of HCl) over  $CuCl_2$  on pumice at 400° (54) or with MeOH over  $Al_2O_3$  at 290° (MeCl (3:7005) is also formed) (55) see indic. refs.]

From 1,2-dichloroethane (3:5130). [For formn. of  $\bar{C}$  (22% yield) together with other prods. from ethylene (di)chloride with  $Cl_2$  in pres. of  $AlCl_3/NaCl/FeCl_3$  at 400–480° see (56).]

From various mixed-halogenated ethanes. [For formn. of  $\bar{C}$  from 1,2-dibromo-1,2-dichloroethane (Beil. 1-93, I<sub>1</sub>-(29), I<sub>2</sub>-(64)) by removal of 2 Br with Zn in alc. (57) or with  $H_2$  over Ni at 300–320° (45) see indic. refs.; from 2-bromo-1,1,2-trichloroethane (by elimination of Br-Cl) with Zn dust in boilg. alc. (58) (59) or from 2-iodo-1,1,2-trichloroethane on distn. at atm. press. (60) see indic. refs.]

From acetylene. With chlorine. [Starting from acetylene the addition of 1 mole of  $Cl_2$  yields  $\bar{C}$  to which further addn. of  $Cl_2$  gives 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750), for this reason most of the processes for prepn. of the latter cpd. by this method yield (or may be made to yield)  $\bar{C}$  as a by-product. Since the patents on the addn. of chlorine to acetylene have been extensively cited under the text of 1,1,2,2-tetrachloroethane (3:5750) (prepn. from acetylene), refer to that compound; however, see also (61) (62) (63).]

With other reagents. [For formn. of  $\bar{C}$  from acetylene with  $SbCl_3$  (64) (65) cf. (57), with  $SbCl_3$  +  $SbCl_5$  (66), or with aq. ICl soln. (57), see indic. refs.]

### CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis of  $\bar{C}$ . [ $\bar{C}$  in s.t. at 360° for 10 hrs. is completely decomposed (64) into carbon + HCl.] (See also above under detn. of  $\bar{C}$ .)

Oxidation of  $\bar{C}$ . [ $\bar{C}$  with  $O_2$  in pres. of suitable cat. (e.g.,  $Br_2$  or  $H_2SO_4$ ) gives (67)

chloroacetyl chloride (3:5235). —  $\bar{C}$  with  $O_2 + N_2$  in ultra-violet light evolves HCl but yields (68) only resinous (perhaps polymerization) products.]

[For study of rate of reactn. of  $\bar{C}$  (in AcOH) with  $O_3$  see (69).]

[Note that  $\bar{C}$  with  $NH_3 +$  air over Pt/Rh cat. at 820–850° gives (70) HCN.]

[ $\bar{C}$  with air over (strongly chlorinated) CuO at 450° gives (76) much phosgene (3:5000).]

Stabilization of  $\bar{C}$ . [For stabilization of  $\bar{C}$  by addn. of small amts. of alc.  $NH_3$  (71), with  $Et_3N$  (72), or with various phenols, amines, and aminophenols (73), see indic. refs.] (See also under corresp. subtopic of 1,1,2-trichloroethylene (3:5170).)

Polymerization of  $\bar{C}$ . [ $\bar{C}$  in the pres. of dibenzoyl peroxide (or other org. peroxides) on htg. under press. reacts with itself yielding mainly (74) a dimer, viz., 1,3,4,4-tetrachlorohutene-1 (3:9058), accompanied by other prods.]

[For study of influence of radiation of 1980–1860 Å (from Al aro) and accompanying polymerization see (75).]

Reaction with halogens. *Behavior of  $\bar{C}$  with  $Cl_2$* . [ $\bar{C}$  adds 1 mole  $Cl_2$  giving (69% yield (58)) 1,1,2,2-tetrachloroethane (3:5750); for study of this reactn. in light of 4360 Å see (77).] (See also under the individual *cis*- (3:5042) and *trans*- (3:5028) stereoisomers)

*Behavior with  $Br_2$* . [ $\bar{C}$  adds 1 mole  $Br_2$  giving (60) (57) 1,2-dibromo-1,2-dichloroethane [Beil. I-93, I<sub>1</sub>-(29), I<sub>2</sub>-(64)], h.p. 195° at 760 mm. (78) (59), h.p. 79.0–79.5° at 15 mm. (79); for study of photochem. addn. of  $Br_2$  in gas phase (80) (81) and in  $CCl_4$  soln. (81) (82) in sunlight (83) (84) see indic. refs.]

*Behavior with  $ICl$* . [ $\bar{C}$  in  $CHCl_3$  adds  $ICl$  in sunlight yielding (60) 2-iodo-1,1,2-trichloroethane, b.p. 77° at 0 mm.,  $D_4^{15} = 2.2760$  (60).]

. Reaction with halogen hydrides. *Reaction with  $HCl$* . [ $\bar{C}$  in the absence of cat. does not add dry  $HCl$ ;  $\bar{C}$  with dry  $HCl$  in the pres. of small amts.  $AlCl_3$  at 30–40° gives (87% yield (86)) (85) (104) 1,1,2-trichloroethane (3:5330) accompanied (85) by 1,1,2,3,4-pentachlorobutane (3:0750); this latter prod. and doubtless various others appear to be formed in the pres. of the  $AlCl_3$  by various condensations among the various organic materials (see below).]

Reaction with  $H_2SO_4$ . [ $\bar{C}$  is only slightly attacked at 20° by either 85% or 96%  $H_2SO_4$  and no polymerization occurs (87); on running the  $H_2SO_4$  layer into 10 vols. of cold aq. qual. evidence of formn. of chloroacetaldehyde (3:7212) was obt'd. (87). —  $\bar{C}$  with conc.  $H_2SO_4$  is unchanged up to 120° but at higher temps. carbonizes without evidence of formn. of chloroacetaldehyde (88).]

[However,  $\bar{C}$  with fuming  $H_2SO_4$  (50%  $SO_3$ ) or  $\bar{C}$  with  $SO_3$  followed by aq. gives (88) (89) chloroacetaldehydesulfonic acid from which htg. with 80%  $H_2SO_4$  gives (88) (89) chloroacetaldehyde (3:7212).]

*Behavior with alkali*. [ $\bar{C}$  with alc. KOH (90) (91) loses 1 HCl yielding chloroacetylene (3:7000); this prod. sometimes (92) (93) causes spontaneous ignition of the system especially when its alc. soln. comes in contact with air in cleaning the reaction flask (91).] (See also under the individual *cis*- (3:5042) and *trans*- (3:5028) stereoisomers.)

[Note that  $\bar{C}$  with alc. NaSH does not react even after 6 hrs. reflux. (92).]

*Behavior with  $NH_3$* . [ $\bar{C}$  with liq.  $NH_3$  under high press. reacts only very slightly although a small amt. of chloroacetylene (3:7000) (from loss of HCl) is formed (94).]

*Behavior with metals*. [For study of corrosion of common metals by  $\bar{C}$  see (5).]

*Behavior with other inorganic reactants*. [ $\bar{C}$  with liq. nitryl chloride ( $ClNO_2$ ) in s.t. at 100° for 3 hrs. gives by addn. to unsat'd. linkage (67% yield (95)) 2-nitro-1,1,2-trichloroethane, pale yel. oil, h.p. 63° at 13 mm. —  $\bar{C}$  cautiously added to 4 vols. of a mixt. of conc. + fmg.  $HNO_3$  and warmed gives (96) a small amt. of nitro-trichloromethane (chloropierin). —  $\bar{C}$  with liq.  $N_2O_4$  at ord. temp. for 24 hrs. in an unsealed tube (use of sealed tube leads to serious explosions) reacts (96) to give a little oxalic acid dihydrate (1:0445) together with an unidentified lachrymatory oil.]

## BEHAVIOR WITH ORGANIC REACTANTS

With hydrocarbons.  $\bar{C}$  (1 mole) with cyclopentadiene (1 mole) (1:8030) in s.t. at 180–190° for 15 hrs. yields (97) two Diels-Alder type adducts. — For reactn. of  $\bar{C}$  with  $C_6H_6$  + Al/Hg see under individual *cis*- (3:5042) and *trans*- (3:5028) stereoisomers]

With other chlorinated hydrocarbons. (For reaction of  $\bar{C}$  with itself see above under polymerization.)

With methylene (di)chloride (3:5020).  $\bar{C}$  (1 wt. pt.) with  $CH_2Cl_2$  (3 wt. pts.) +  $AlCl_3$  (0.3 wt. pt.) at 40° for 8 hrs. gives (24% yield (98)) 1,1,2,3-tetrachloropropane (3:6035)].

With chloroform (3:5050).  $\bar{C}$  (1 wt. pt.) with  $CHCl_3$  (3 wt. pts.) +  $AlCl_3$  (0.25 wt. pt.) stirred with sand for 20 hrs. at 30° (99) cf. (100) (101) (102) gives (yields: 63% (99), 70–75% at 50° (100), 46% at 17° in 22 hrs. (100)) 1,1,2,3,3-pentachloropropane (3:6280)]

With carbon tetrachloride (3:5100).  $\bar{C}$  with  $CCl_4$  +  $AlCl_3$  gives (101) (102) cf. (103) 1,1,1,2,3,3-hexachloropropane (3:6460); for reactn. of this system yielding heptachloropentenes see (103)]

With 1,1,2-trichloroethane (3:5330).  $\bar{C}$  with 1,1,2-trichloroethane +  $AlCl_3$  (1%) at 35–40° for 5 days gives (104) two diastereoisomeric 1,1,2,3,4-pentachlorobutanes, viz., liq. (3:9068) and solid (3:0750).]

With 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750).  $\bar{C}$  with acetylene tetrachloride +  $AlCl_3$  gives a mixt. from which can be isolated only (104) solid 1,1,2,3,4-pentachlorobutane (3:0750).]

With 1,1,1,2-tetrachloroethane (3:5555).  $\bar{C}$  with unsym.-tetrachloroethane +  $AlCl_3$  at 40° for 10 days gives (104) 1,1,1,4,4-pentachlorobutene-2 (3:9054).]

With pentachloroethane (3:5880).  $\bar{C}$  with pentachloroethane +  $AlCl_3$  at 40° for 12 days presumably first forms both 1,1,2,2,3,4,4-heptachlorobutane (3:9056) and 1,1,1,2,3,4,4-heptachlorobutane, but the latter loses HCl and by further reaction and/or resinification is lost in the accompanying resins (104); the HCl thus split out adds (in the pres. of  $AlCl_3$ ) to  $\bar{C}$  yielding 1,1,2-trichloroethane which then condenses with more  $\bar{C}$  as stated above (104).]

With hexachloropropene (3:6370).  $\bar{C}$  with hexachloropropene +  $AlCl_3$  in  $CH_2Cl_2$  soln. yields (105) a single 1,1,2,2,3,3,4,5,5-octachloropentene-1, b.p. 145–147° at 11 mm., 113–113.5° at 2 mm.,  $D_4^{25} = 1.749$ ,  $n_D^{25} = 1.5607$  (105). This prod. with conc.  $H_2SO_4$  gives (80% yield (105)) a mixt. of pentachlorobutenecarboxylic acids (105).]

Behavior with organic OH or SH derivs.  $\bar{C}$  (1 mole) with  $C_2H_5SH$  (2 moles) in alc. KOH (2.6 moles) refluxed  $\frac{1}{2}$  hr. gives (yield not stated (106)) 1,2-bis-(ethylthio)ethylene, b.p. 176° at 13 mm.]

$\bar{C}$  (1 mole) with benzyl mercaptan (2 moles) in alc. KOH refluxed 7 hrs. gives (yield not stated (106)) 1,2-bis-(benzylthio)ethylene, white ndls. from alc. or AcOH, m.p. 61°; this prod. in  $CS_2$  adds 1  $Br_2$  giving 1,2-dibromo-1,2-bis-(benzylthio)ethane, ndls. from ether, m.p. 73–74°.]

$\bar{C}$  (1 mole) with thiophenol (2 moles) in alc. NaOEt (2 moles) refluxed 24 hrs., poured into aq., gives (yield not stated (108)) 1,2-bis-(phenylthio)ethylene, b.p. 235–242° nt 760 mm., pl. from lt. pet., m.p. 62°.]

$\bar{C}$  (1 mole) with *p*-tolylmercaptan (2 moles) in 7% alc. KOH refluxed 3 hrs. gives (90% yield (107)) 1,2-bis-(*p*-tolylthio)ethylene, ndls. from alc., m.p. 93°; this prod. in  $CHCl_3$  adds 1 mole  $Br_2$  giving (100% yield) 1,2-dibromo-1,2-bis-(*p*-tolylthio)ethane, cryst. from pet. ether, m.p. 72° (107).]

[For analogous reactn. with  $\bar{C}$  of *o*-nitrothiophenol or *p*-nitrothiophenol see (106).]

$\bar{C}$  (1 mole) with an alk. salt of thiosalicylic acid (*o*-mercaptobenzoic acid) reacts similarly giving (109) (110) cf. (111) (112) 1,2-bis-(*o*-carboxyphenylthio)ethylene ("S,S'-vinylene-

bis-thiosalicylic acid") [Beil. X-128, X<sub>1</sub>-(55)]; this prod. with KOH/NaOH at 220-230° gives (113) 3-hydroxythionaphthene (thioindoxyl) [Beil. XV11-110, XV11<sub>1</sub>-(60)], or by actn. of acid condensing agents (e.g., fuming H<sub>2</sub>SO<sub>4</sub>, ClSO<sub>3</sub>H, etc.) yields (114) the important dyestuff thioindigo [Beil. XIX-177, XIX<sub>1</sub>-(600)]. — Note that the corresp. condens. of  $\bar{C}$  with salicylic acid (*o*-hydroxybenzoic acid) or with anthranilic acid (*o*-aminobenzoic acid) cannot be effected (112).]

Behavior with other misc. organic reactants. [ $\bar{C}$  with paraformaldehyde (1:0080) + cone. H<sub>2</sub>SO<sub>4</sub> gives (115) a resin (cf. behavior of 1,1,2-trichloroethylene (3:5170)).]

[ $\bar{C}$  (1 mole) with EtMgBr (2 moles) yields (110) C<sub>2</sub>H<sub>6</sub> + BrMgC≡C—MgBr + MgCl<sub>2</sub>.]

[ $\bar{C}$  does not (117) react with acetyl iodide even after 150 days at 25°.]

### COLOR TESTS FOR $\bar{C}$

② Color test with  $\alpha$ -naphthol/cyclohexanol.  $\bar{C}$  (1 drop) with 2 ml. of a 2% soln. of  $\alpha$ -naphthol (1:1500) in cyclohexanol (1:6415) + 2 pellets solid NaOH boiled 25 seconds, cooled, gives after acidification with AcOH or 85% H<sub>2</sub>SO<sub>4</sub>, stdg. 1 min., and shaking a violet or red-violet color (118). — [Note that under these conditions the responso given by methylene (di)chloride (3:5020) is green-blue; by both ClICH<sub>2</sub> (3:5050) and CCl<sub>4</sub> (3:5100) is intense blue; by 1,2-dichloroethane (ethylene dichloride) (3:5130) is colorless to pale green; by 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) is intense green-blue; by pentachloroethane (3:5880) is gray-green; by 1,1,2-trichloroethylene (3:5170) is intense green-blue; and by tetrachloroethylene (3:5460) is green (118).]

— Mercury bis-(chloroacetylde) Hg(—C≡C—Cl)<sub>2</sub>. Shining white pl. from hot CHCl<sub>3</sub>; although reported to melt at 185° (110) (120) (121) has also been found (122) to explode with great violence well below that temperature, i.e., 174-175° (122). [From  $\bar{C}$  with aq. Hg(CN)<sub>2</sub> + KOH on shaking at room temp. (01) (123) for 48 hrs. (119), or from  $\bar{C}$  in alc. run into a stirred aq. soln. of HgCl<sub>2</sub> + NaCN + KOH (120), or from  $\bar{C}$  shaken with an aq. soln. of HgO + NaCN + NaOH (122). — Note, however, that in fact this prod. results only from the higher-boilg. (*cis*) stereoisomer of  $\bar{C}$  (3:5042) and that the lower-boilg. (*trans*) stereoisomer (3:5028) reacts much more slowly and quite differently to yield mercury bis-( $\alpha,\beta$ -dichloroethylenide), m.p. 50.3° (122). — Note further that by the above treatment 1,1,2-trichloroethylene (3:5170) gives mercury bis-(trichloroethylenide), m.p. 83°, but this prod. is much more sol. in CHCl<sub>3</sub> than the analogous material from  $\bar{C}$  (for use in detect. of  $\bar{C}$  in pres. of 1,1,2-trichloroethylene see (123)).]

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## 3:5035 1,1-DICHLOROETHANE

(Ethylidene (di)chloride;

unsym.-dichloroethane)



Bell. I - 83

I-(23)

I-(52)

B.P.

F.P.

57.30° at 760 mm. (1) (2)

-90.6° (1)

 $D_4^{25} = 1.16709$  (1)

57.28-57.34° cor. (3)

-90.7° (2)

 $D_4^{20} = 1.17570$  (1)

57.25° at 760 mm. (4)

-97.4° (8)

1.1755 (8)

57.0-57.1° (5) (6) (7)

-90° (6)

 $D_4^{15} = 1.18350$  (1)

57.1° at 760 mm. (8)

 $n_D^{20} = 1.41038$  (8)

56.7-56.9° at 743 mm. (9)

 $n_D^{15} = 1.41075$  (1)

Liquid. — [For b.p. at various press. from 70-277 mm. see (11).] — Alm. insol. aq. [for precise data see (5) (6) (7) (11).] — [For f.p./compn. data of mixts. with 2,2-dichloropropane (3:7149) see (10).] — [For use as dry cleaning fluid see (12); for use as corrosion inhibitor for alk. on tinned metal see (13).]

Ĉ forms with EtOH (1:6130), b.p. 78.3°, a const.-boilg. mixt., b.p. 54.6°, contg. 88.6 wt. % Ĉ (4); Ĉ forms with isopropyl alc. (1:0135), b.p. 82.45°, a const.-boilg. mixt., b.p. 50.6°, contg. 82 wt. % Ĉ (4); Ĉ forms with *ter*-butyl alc. (1:9140), b.p. 82.5°, a const.-boilg. mixt., b.p. 57.1°, contg. 94 wt. % Ĉ (14); Ĉ forms with acetone (1:5400), b.p. 56°, a const.-boilg. mixt., b.p. 57.55°, contg. 70 wt. % Ĉ (14); Ĉ forms with CS<sub>2</sub>, b.p. 46.3°





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**3:5035 1,1-DICHLOROETHANE**  
(Ethylidene (di)chloride;  
unsym.-dichloroethane)



Beil. I - 83

I<sub>1</sub>-(23)

I<sub>2</sub>-(52)

B.P.

F.P.

57.30° at 760 mm. (1) (2)

-96.6° (1)

$D_4^{25} = 1.16790$  (1)

57.28-57.34° cor. (3)

-96.7° (2)

$D_4^{20} = 1.17570$  (1)

57.25° at 760 mm. (4)

-97.4° (8)

1.1755 (8)

57.0-57.1° (5) (6) (7)

-99° (9)

$D_4^{15} = 1.18350$  (1)

57.1° at 760 mm. (8)

$n_D^{20} = 1.41638$  (5)

56.7-56.9° at 743 mm. (9)

$n_D^{15} = 1.41975$  (1)

Liquid. — [For h.p. at various press. from 70-277 mm. see (11).] — Alm. insol. aq. [for precise data see (5) (6) (7) (11).] — [For f.p./compn. data of mixts. with 2,2-dichloropropane (3:7140) see (10).] — [For use as dry cleaning fluid see (12); for use as corrosion inhibitor for alk. on tinned metal see (13).]

$\bar{C}$  forms with EtOH (1:6130), b.p. 78.3°, a const.-boilg. mixt., b.p. 54.6°, contg. 88.5 wt. %  $\bar{C}$  (4);  $\bar{C}$  forms with isopropyl alc. (1:6135), b.p. 82.45°, a const.-boilg. mixt., b.p. 56.6°, contg. 82 wt. %  $\bar{C}$  (4);  $\bar{C}$  forms with *ter*-butyl alc. (1:6140), h.p. 82.5°, a const.-boilg. mixt., b.p. 57.1°, contg. 94 wt. %  $\bar{C}$  (14);  $\bar{C}$  forms with acetone (1:5400), b.p. 56°, a const.-boilg. mixt., b.p. 57.55°, contg. 70 wt. %  $\bar{C}$  (14);  $\bar{C}$  forms with  $\text{CS}_2$ , h.p. 46.3°

const.-boil. mixt., b.p. 44.75°, contg. about 28 wt. %  $\bar{C}$  (14). [For study of b.p.,  $D$ , and vapor-liq. equil. of binary mixts. of  $\bar{C}$  with  $\text{CHCl}_3$  (3:5050),  $\text{CCl}_4$  (3:5100), or with 1,2-dichloroethane (3:5130) see (27).]

[For soly. of aq. in  $\bar{C}$  see (29); for adsorption of  $\bar{C}$  by activated carbon at various temps. see (30).]

[For prepn of  $\bar{C}$  from acetaldehyde (1:0100) with  $\text{PCl}_5$  see (15) (16) (17); from vinyl chloride (3:7010) by catalyzed addn. of  $\text{HCl}$  see (18) (19) (20) (note that in absence of catalyst addn. of  $\text{HCl}$  to vinyl chloride is very slow (21)); for formn. of  $\bar{C}$  (22.6%) together with other products from ethane with  $\text{Cl}_2$  above 290° in pres. of ethylene see (28).]

$\bar{C}$  on passing over pumice at dark red heat yields (22) (23) vinyl chloride (3:7010) +  $\text{HCl}$ .

[For reactn. of  $\bar{C}$  +  $\text{AlCl}_3$  with 1,2-dichloroethylene (3:5030) or with trichloroethylene (3:5170) yielding polychlorobutanes see (24); for reactn. of  $\bar{C}$  with amylidene disodium see (25).]

$\bar{C}$  on htg. in s.t. at 120° with aq. alc. soln. of 2 moles  $\text{Na}$  (or  $\text{K}$ )  $\alpha$ -naphtholate yields (26) acetaldehyde di- $\alpha$ -naphthylacetal, ndls., m.p. 117° (26).

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3:5042 <i>cis</i> -1,2-DICHLOROETHYLENE ( <i>cis</i> -Acetylene dichloride)		$\begin{array}{c} \text{H}-\text{C}-\text{Cl} \\   \\ \text{H}-\text{C}-\text{Cl} \end{array} \quad \text{C}_2\text{H}_2\text{Cl}_2$		Beil. I — I <sub>1</sub> -(78) I <sub>2</sub> -(159)
B.P.		F.P.		
60.33–60.38° eor.	(1)	–82°	(22) $D_4^{25} = 1.2743$	(12)
60.25° at 760 mm.	(2) (3) (4)	–81°	(17) $D_4^{20} = 1.2820$	(12)
60.2° at 760 mm.	(5)	–80.5°	(3) $D_4^{15} = 1.2913$	(2)
60.14°	(6)			1.2896 (12)
60.1°	(7)			
60.0–60.5°	(8) (9)			$n_D^{25} = 1.44284$ (11)
59.9–60.1° at 760 mm.	(10)			$n_D^{17} = 1.44992$ (15)
59.9° at 768 mm.	(11)			$n_D^{15} = 1.45189$ (3)
59.8° at 763 mm.	(12)			
59.6° at 745 mm.	(13)			
59.5–60.1° at 753 mm.	(14)			
59.4–59.7° at 749.6 mm.	(15)			
59.4–60.4°	(39)			
50°	(16)			

See also both *trans*-1,2-dichloroethylene (3:5028) and ordinary (mixture of *cis* and *trans*) 1,2-dichloroethylene (3:5030); the following text is restricted to studies on substantially pure *cis*-stereoisomer.

Note carefully that 1,2-dichloroethylene is *not* the same as ethylene (di)chloride (3:5130) (there are an almost incredible number of errors in the literature involving this point); neither is it the same as the now very important 1,1-dichloroethylene (vinylidene (di)chloride) (3:5005).

### GENERAL DATA ON $\bar{C}$

Note that substantially pure  $\bar{C}$  is commercial solvent in U.S.A. under designation "Di-60" (referring to the two chlorine atoms and the b.p.) [for study of thermal conductivity and for tabulation of constants of comml.  $\bar{C}$  see (18). — For toxicity of  $\bar{C}$  see (40) (23). — For use of  $\bar{C}$  in extraction of caffeine from coffee see (24)].

[For data on vap. press. of  $\bar{C}$  over temp. range 27–59.8° see (12). — For data on flammability of  $\bar{C}$  see (19). — For ebullioscopic constant of  $\bar{C}$ , viz., 34.4° (for 1 mole solute in 100 g.  $\bar{C}$ ), see (20).]

Binary systems contg.  $\bar{C}$ . (See also below under azeotropes.) — [ $\bar{C}$  + *trans*-1,2-dichloroethylene (3:5028): for use of  $n_D^{25}$  in detn. of composition of mixt. see (11); for f.p./compn. data (eutectic, f.p. –91°, contg. about 71%  $\bar{C}$ ) see (17). — For f.p./compn. data on binary systems  $\bar{C}$  + ethylene (di)chloride (3:5130),  $\bar{C}$  + 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750), or  $\bar{C}$  + ethylene (di)bromide see (17). — For study of soly. of various other *cis/trans* isomers in  $\bar{C}$  see (5).]

Quaternary systems contg.  $\bar{C}$ . [For study of system contg.  $\bar{C}$  +  $\text{CHCl}_3$  (3:5050) + trichloroethylene (3:5170) +  $\text{EtBr}$  (eutectic, f.p. –139.1°, contg. 13.8 wt. %  $\bar{C}$  + 19.7 wt. %  $\text{CHCl}_3$  + 21.6 wt. % trichloroethylene + 44.9 wt. %  $\text{EtBr}$  recommended as a non-inflammable mixt. for low-temp. cryostats) see (22); for mixt. of the above four compds. + methylene dichloride (3:5020) (similarly recommended) see (22).]

Azeotropes contg.  $\bar{C}$ . Binary azeotropes —  $\bar{C}$  with aq. forms a const.-boilg. mixt., b.p. 55.3°, contg. 96.65%  $\bar{C}$  (41) (42). —  $\bar{C}$  with  $\text{EtOH}$  (1:6130) forms a const.-boilg. mixt., b.p. 57.7° at 760 mm. (21) (41) (42), contg. 90.20%  $\bar{C}$  (41) (42) = 81.4 mole %  $\bar{C}$  (21)

Ternary azeotropes.  $\bar{C}$  with  $\text{EtOH}$  (1:6130) + aq. forms a const.-boilg. mixt., b.p. 53.8°, contg. 90.50%  $\bar{C}$  + 6.65%  $\text{EtOH}$  + 2.85% aq. (41) (42).

PREPARATION OF  $\bar{C}$ 

Pure  $\bar{C}$  is usually obtd. by careful fractional distillation at ord. press. of the mixt. of *cis* and *trans* stereoisomers comprising ord. 1,2-dichloroethylene (3:5030) [for brief comments on this mode of sepn. see (1) (2) (6) (7) (8) (9) (10) (11) (13) (15) (27)]; note that some workers (13) recommend distn. in atmosphere of  $CO_2$ . — For detn. of the % compn. of mixts. of  $\bar{C}$  with its stereoisomer by means of  $n_D^{25}$  see (11); by means of dielectric const. see (13) (27)].

[For study of possibility of sepn. of  $\bar{C}$  from its stereoisomer by differential adsorption on silica gel see (25).]

[For prepn. of  $\bar{C}$  from pure *trans* stereoisomer (3:5028) by isomerization with 6 wt. %  $Br_2$  in dark for 24 hrs. followed by subsequent fractionation of the resultant mixt. see (11).]

ISOMERIZATION OF  $\bar{C}$ 

$\bar{C}$  under the influence of heat, light, or various catalysts in part isomerizes to *trans*-1,2-dichloroethylene (3:5028). — [For study of thermal isomerization of  $\bar{C}$  in vapor phase nt 185–275° (26), up to 350° (27), up to 975° (28), in liquid phase or in various solutions (13) see indic. refs.; note that the equilibrium mixt. nt 300° conts.  $60.8 \pm 0.7\%$   $\bar{C}$ , at 350° conts.  $59.4 \pm 0.3\%$   $\bar{C}$  (27), at 975° conts.  $52.3\%$   $\bar{C}$  (28) — For study of kinetics of thermal isomerization see (29).]

[For patent on isomerization of pure  $\bar{C}$  to a mixt. contg. 18% *trans* stereoisomer by means of a small amt.  $Br_2$  at 30° or above in pres. of cat. or in vapor phase at not over 300° see (30).]

CHEMICAL BEHAVIOR OF  $\bar{C}$ 

Reactions with inorganic compds.  $\bar{C}$  (in vapor phase at 95° in light of 4360 Å (31)) with  $Cl_2$  (in absence of  $O_2$ ), or  $\bar{C}$  as liquid with  $SO_2Cl_2$  (1½ moles) in pres. of trace of dibenzoyl peroxide refluxed 3 hrs. in dark (8), adds 1 mole halogen giving (85% yield (8)) 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750).

$\bar{C}$  with  $Br_2$  in sunlight adds 1 mole halogen yielding (2) (32) 1,2-dibromo-1,2-dichloroethane [Beil. I-93, I<sub>1</sub>-(29), I<sub>2</sub>-(64)], b p. 195° at 760 mm. (3) (33), b.p. 79.0–79.5° at 15 mm. (2). — [For extensive study of influence of  $O_2$  and other factors see (32); for study of kinetics in  $CCl_4$  soln. see (2) (34) (35); note that rate of addn. of  $Br_2$  either directly or in  $CCl_4$  is half as great as for the stereoisomeric *trans* form (3:5028) but that it is increased in pres. of  $SbBr_3$  (35).]

$\bar{C}$  in the absence of  $AlCl_3$  or other cat. does not add dry  $HCl$ ; satn. of  $\bar{C}$  with dry  $HCl$  changes  $n_D^{25}$  by an amount corresp. to only 2% change in compn. (11).

[ $\bar{C}$  with alc.  $KOH$  splits out 1  $HCl$  yielding chloroacetylene (3:7000); note that this reactn. is about 20 times as fast for  $\bar{C}$  as for its *trans* stereoisomer (2) ]

$\bar{C}$  with aq.  $NaOH/Hg(CN)_2$  behaves quite differently from its *trans* stereoisomer (3:5028): on shaking at room temp. with specified concns. (16)  $\bar{C}$  begins to react within 30 min., losing 1  $HCl$  and pptg. mercuric bis-(chloroacetylde),  $Hg(-C\equiv C-Cl)_2$ ; this prod. cryst. from  $CHCl_3$  (36) (37) (38) in white shining pl. with characteristic acetylene-like odor and although alleged to melt at 185° (36) (37) has also been found to explode with great violence well below that temp., i.e., 174–175° (16).

Reactions with organic compds. [ $\bar{C}$  with  $C_6H_6 + Al/Hg$  nt 0° gives same prods. as does the ordinary (mixture) 1,2-dichloroethylene (3:5030) (presumably indicating partial isomerization of  $\bar{C}$ ); these prods. include dibenzyl, triphenylethane, tetraphenylethane, etc. (15).]

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3:5050 CHLOROFORM  
(Trichloromethane)

CHCl<sub>3</sub>      Boil. I - 61  
I<sub>1</sub> - (9)  
I<sub>2</sub> - (14)

B.P.	F.P.	
[62.0° at 760 mm. (2)]	-63.0° (27)	$D_4^{30} = 1.47060$ (12)
	(28) (61)	$n_D^{25} = 1.44295$ (49)
[61.97° at 760 mm. (3)]	-63.2° (29)	$D_4^{25} = 1.47988$ (12)
	(26)	1.47972 (20)
[61.64° at 760 mm. (4)]	-63.3° (30)	1.47955 (45)
	(1)] -63.41° (31)	1.4794 (43)
[61.40° at 758 mm. (5)]	-63.495° (32)	1.4793 (44)
61.36-61.38° at 763.9 mm. (6)	-63.5° (33)	1.4791 (21)
	(34) (35) (36)	1.4789 (19)
	(37) (12) (38)	1.4702 (46)
61.33-61.38° at 760 mm. (7)	-63.57° (17)	$n_D^{25} = 1.44460$ (50)
61.3° u.c. at 759 mm. (8)	-63.6° (39)	1.4433 (51)
61.28° at 761 mm. (9)	-63.7° (40)	1.4431 (19)
61.20-61.25° at 760 mm. (10)	-64.19° (41)	1.44309 (52)
61.21° at 760 mm. (11)	-66.5° (42)	1.4424 (44)
61.20° at 760 mm. (12)		$n_D^{24.5} = 1.4437$ (43)
	(1) (15) (16) See Note 2.	$n_D^{22.4} = 1.44500$ (53)

B.P. (contd.)

61.152°	at 760 mm. (13)	$D_4^{20} = 1.48921$ (13)
61.15°	at 760 mm. (14)	1.48917 (12)
61.09°	at 760 mm. (17)	1.48913 (13)
61.07-61.09°	at 760 mm. (18)	1.48901 (13)
61.05-61.10°	at 760 mm. (50)	1.4890 (47)
61.05-61.10°	at 758 mm. (19)	1.4889 (10)
61.0°	(20)	(48)
61.0°	at 755 mm. (21)	1.4817 (62)
60.94-60.96°	at 755 mm. (22)	$n_D^{20} = 1.44637$ (10)
60.93°	at 744.2 mm. (4)	1.4458 (7)
60.9°	at 754.3 mm. (23)	1.446 (17)
60.9°	at 732 mm. (24)	$D_4^{18.85} = 1.4828$ (54)
60.7°	at 743.8 mm. (25)	$n_D^{18.85} = 1.44572$ (54)
60.39°	at 735.6 mm. (4)	$D_4^{15} = 1.49845$ (12)
56.0°	at 664 mm. (21)	1.4963 (21)
55.10°	at 632.8 mm. (26)	$n_D^{15} = 1.44858$ (12)
53.8°	at 616 mm. (21)	1.4466 (55)
50.6°	at 550 mm. (21)	$n_D^{12.5} = 1.4506$ (56)
47.0°	at 481 mm. (21)	
42.8°	at 416 mm. (21)	
40.40°	at 371.8 mm. (26)	
38.0°	at 342 mm. (21)	
33.0°	at 287 mm. (21)	
28.115°	at 221.8 mm. (26)	
27.0°	at 223 mm. (21)	

See Note 1.

See Note 3.

Note 1. For b.p. of  $\tilde{C}$  at various pressures from 355-2347 mm. see (13); for vap. press. of  $\tilde{C}$  over range  $-62.1^\circ$  to  $0^\circ$  (57) or  $-64.2^\circ$  to  $-10.7^\circ$  (58) see indic. refs.

Note 2. For influence of high press. on m.p. of  $\tilde{C}$  see (33); for study of rate of solidification see (35).

Note 3. For  $D_4^I$  over range  $-61.3^\circ$  to  $+59.8^\circ$  see (59).

[For extraordinarily comprehensive reviews of the history and general chemistry of  $\tilde{C}$  see (1) (60).]

[See also methylene (di)chloride (3:5020) and carbon tetrachloride (3:5100).]

## MISCELLANEOUS PHYSICAL PROPERTIES OF $\tilde{C}$

### VARIOUS SOLUBILITY RELATIONS

With water.  $\tilde{C}$  is only very slightly sol. aq. and is eas. volat. with steam; e.g., 100 g. aq. at  $15^\circ$  dissolves 9.852 g.  $\tilde{C}$  (18); water satd. with  $\tilde{C}$  conts. at  $20^\circ$  0.8%  $\tilde{C}$  (63) cf. (64). For studies of soly. of aq. in  $\tilde{C}$  at  $9^\circ$  (65),  $20^\circ$  (63),  $25^\circ$  (65), and  $30^\circ$  (65) see indic. refs.; note that at  $20^\circ$   $\tilde{C}$  satd. with aq. conts. 99.8%  $\tilde{C}$  and has  $D_4^{20} = 1.486$  (63).

With various inorganic compounds. [For data on soly. in  $\tilde{C}$  of  $H_2$  (66),  $O_2$  (78),  $HCl$  (67) (68) (69) (79),  $HBr$  (68) (69),  $H_2S$  (67),  $NH_3$  (67),  $CO_2$  (70) (80) (81),  $N_2O$  (81), and  $NO_2$  (70) see indic. refs. — For data on soly. of  $I_2$  in  $\tilde{C}$  see (71) (72) (73) (74); for study of nature of  $I_2$  solns. in  $\tilde{C}$  see (75); for soly. of  $I_2$  in vapor of  $\tilde{C}$  see (76).]

With organic materials. [For study of absorption of vapor of  $\tilde{C}$  by kerosene see (77).]

BINARY SYSTEMS CONTAINING  $\bar{C}$ (See also azotropes containing  $\bar{C}$ )

$\bar{C}$  with various inorganic compounds.  $\bar{C}$  + *aq.*: for soly. data and diag. see (64); note that a previously described (82) hydrate of  $\bar{C}$  could not be confirmed (64). —  $\bar{C}$  +  $Cl_2$ : for f.p./compn. data and diag. (note that 4 different compounds are formed) see (34). —  $\bar{C}$  +  $Br_2$ : for f.p./compn. data and diag. see (34) (36) (note that no compds. are formed and that eutectic has m.p.  $-72^\circ$  (34) with about 86 mole %  $\bar{C}$ ).

$\bar{C}$  with org. cpds. of Order 1.  $\bar{C}$  + *n-hexane* (1:8530): for f.p./compn. data see (83); for densities over range  $-90^\circ$  to  $+60^\circ$  see (85). —  $\bar{C}$  +  $C_6H_6$  (1:7400): for f.p./compn. data and diag. see (38); for  $D_4^{25}$ /compn. and  $n_D^{25}$ /compn. data over entire range see (19); for  $D_{25}^{25}$ /compn. data see (18); for liq. vapor equil. see (19) (117) (112) (124). —  $\bar{C}$  + *toluene* (1:7405): for f.p./compn. data see (83); for data on specific gravity of system from 15–25° see (86); for study of liq.-vapor equil. see (123). —  $\bar{C}$  + *cyclohexane* (1:8405): for f.p./compn. data see (83); for  $D_4^{20}$  compn. see (47).

$\bar{C}$  + *MeOH* (1:6120): for f.p./compn. data see (37) (84); for  $D_4^{25}$ /compn. and  $n_D^{25}$ /compn. see (44). —  $\bar{C}$  + *EtOH* (1:0130): for  $D_4^{25}$ /compn. data see (45) (46). —  $\bar{C}$  + *benzyl alc.* (1:6480): for density/compn. data over entire range see (87).

$\bar{C}$  + *diethyl ether* (1:6110): for f.p./compn. data and diag. see (42) (88); for  $D_4^{20}$ /compn. see (47). —  $\bar{C}$  + *diisopropyl ether* (1:6125): for  $D_4^{20}$ /compn. see (47). —  $\bar{C}$  + *dioxane-1,4* (1:6400): for  $D_4^{20}$ /compn. see (47). —  $\bar{C}$  + *ethylene glycol dimethyl ether* (1:6141): for study of heat of mixing see (89). —  $\bar{C}$  + *tetraethylene glycol dimethyl ether*: for study of heat of mixing see (89).

$\bar{C}$  + *dimethyl carbonate* (1:3046): for  $D_4^{25}$ /compn. data see (20). —  $\bar{C}$  + *diethyl carbonate* (1:3150): for  $D_4^{25}$ /compn. data see (20).

$\bar{C}$  + *acetone* (1:5400): for f.p./compn. data see (27); for  $D_4^{20}$ /compn. (47),  $D_4^{25}$ /compn. (10) (46),  $n_D^{25}$ /compn. (19), and  $n_D^{25.4}$ /compn. (49) data see indic. refs.; for refractive index/compn. for light of various wave lengths see (52).

With org. cpds. of Order 2.  $\bar{C}$  + *nitrobenzene*: for f.p./compn. data and diag. (eutectic, f.p.  $-71.0^\circ$  conts. 81.5 wt. %  $\bar{C}$ ) see (61). —  $\bar{C}$  + *aniline*: for f.p./compn. data and diag. see (27). —  $\bar{C}$  + *N,N*-dimethylaniline: for  $D_4^{25}$ ,  $D_4^{40}$ ,  $n_D^{24.8}$ , and  $n_D^{30.5}$  over entire range of composition see (43). —  $\bar{C}$  + *quinoline*: for  $D_4^{20}$ /compn. data see (47).

With org. cpds. of Order 3.  $\bar{C}$  +  $CH_2Cl_2$  (3:5020): for f.p./compn. data and diag. (eutectic, f.p.  $-108.4^\circ$  conts. 29.5 wt. %  $\bar{C}$ ) see (39); for data on b.p.,  $D_4^{20}$ , and liq.-vapor equil. see (90). —  $\bar{C}$  +  $CCl_4$  (3:5050): for f.p./compn. data and diag. (eutectic, f.p.  $-81.4^\circ$  conts. 50.6 wt. %  $\bar{C}$  (39)) (36) (83) (91) see indic. refs.; for  $D_4^{20}$ /compn. (48) (90),  $D_{25}^{25}$ /compn. (8), b.p. and liq.-vapor equil. (90) see indic. refs. —  $\bar{C}$  + *1,1-dichloroethane* (3:5035): for b.p.,  $D_4^{20}$ , and liq.-vapor equil. see (90). —  $\bar{C}$  + *1,2-dichloroethane* (3:5130): for data on vap. press. (92) and liq.-vap. equil. (93) see indic. refs. —  $\bar{C}$  + *1,1,1-trichloroethane* (3:5058): for f.p./compn. data see (94). —  $\bar{C}$  + *1,1,2-trichloroethylene* (3:5170): for f.p./compn. data and diag. (eutectic, f.p.  $-100.2^\circ$ , conts. 31.2 wt. %  $\bar{C}$ ) see (39). —  $\bar{C}$  +  $\beta,\beta'$ -dichlorodiethyl ether (3:6025): for  $D_4^{20}$ /compn. data see (47).

With org. cpds. of higher orders.  $\bar{C}$  + *1,2-dibromoethane*: for  $D_4^{20}$ /compn. data see (47). —  $\bar{C}$  +  $CBR_4$ : for f.p./compn. data and diag. see (91). —  $\bar{C}$  +  $CHI_3$ : for vap. press. data see (95). —  $\bar{C}$  +  $CS_2$ : for f.p./compn. data see (83); for  $D_{15}^{15}$  compn. (96) or  $D_{25}^{25}$ /compn. (8) see indic. refs.; for liq.-vapor equil. data see (97).

TERNARY SYSTEMS CONTAINING  $\bar{C}$ (See also azeotropes containing  $\bar{C}$ )

$\bar{C}$  + acetone (1:5400) +  $H_2O$ : for studies of liq. equil. at 25° see (98) (99) (100) (101) (102). —  $\bar{C}$  + acetone (1:5400) +  $MeOH$  (1:6120): for ternary b.p. diag. see (103). —  $\bar{C}$  + acetone (1:5400) + diethyl ether (1:6110): for data on refraction see (104). —  $\bar{C}$  + acetone (1:5400) + diisopropyl ether (1:6125): for ternary b.p. diag. see (103).

$\bar{C}$  + acetone (1:5400) +  $C_2H_6$  (1:7400): for ternary b.p. diag. see (103) (19) (105); for refractive data see (104).

$\bar{C}$  + acetone (1:5400) +  $CH_2Cl_2$  (3:5020): for ternary b.p. diag. see (103).

$\bar{C}$  + acetic acid (1:1010) + aq.: for studies of liq. equil. at 25° see (104) (106) cf. (99). —  $\bar{C}$  + acetic acid + lubricating oil: for studies of liq. equil. at 25° see (107).

$\bar{C}$  +  $CH_2Cl_2$  (3:5020) +  $CCl_4$  (3:5100): eutectic, f.p.  $-111.4^\circ$ , conts. 27 wt. %  $\bar{C}$  + 60 wt. %  $CH_2Cl_2$  + 13 wt. %  $CCl_4$  (39).

QUATERNARY SYSTEMS CONTAINING  $\bar{C}$ 

$\bar{C}$  + acetone (1:5400) +  $AcOH$  (1:1010) + aq.: for study of liq. equil. at 25° see (100); for study of use of system in mixed solv. extraction of lubricating oils see (107) (108). —  $\bar{C}$  + trans-1,2-dichloroethylene (3:5028) + 1,1,2-trichloroethylene (3:5170) +  $C_2H_5Br$ : eutectic, f.p.  $-139.1^\circ$ , conts. 17.7 wt. %  $\bar{C}$  + 13.8 wt. % trans-1,2-dichloroethylene + 21.6 wt. % trichloroethylene + 44.9 wt. %  $C_2H_5Br$  (39).

BINARY AZEOTROPES CONTAINING  $\bar{C}$ 

$\bar{C}$  +  $H_2O$ :  $\bar{C}$  forms with aq. a const.-boilg. mixt., b.p.  $56.1^\circ$ , contg. 97.5 wt. %  $\bar{C}$  (14).

$\bar{C}$  +  $MeOH$  (1:6120):  $\bar{C}$  forms with  $MeOH$  a const.-boilg. mixt., b.p.  $53.5^\circ$  (103) (109), contg. 87.5 wt. % (103) = 65 mole % (109)  $\bar{C}$ , cf. also (110) (111) (4) (112) (113). —  $\bar{C}$  +  $EtOH$  (1:6130):  $\bar{C}$  forms with  $EtOH$  a const.-boilg. mixt., b.p.  $59.3^\circ$  at 760 mm. (111),  $59.35^\circ$  at 760 mm. (14), contg. 93.2 wt. %  $\bar{C}$  (111) cf. (14) = 84 mole %  $\bar{C}$  (111) (see also (4) (110)) of  $D_{15}^{15} = 1.4112$  (14); study of liq.-vap. equil. see (45).

alc. a const.-boilg. mixt., b.p. 60

mole %  $\bar{C}$  (111). —  $\bar{C}$  + formic acid (1:1005):  $\bar{C}$  forms with formic acid a const.-boilg. mixt., b.p.  $50.15^\circ$  at 760 mm. (115), contg. 85 wt. %  $\bar{C}$  (115). —  $\bar{C}$  + ethyl formate (1:3000):  $\bar{C}$  forms with ethyl formate a const.-boilg. mixt., b.p.  $62.8^\circ$  (116),  $62.7^\circ$  (111) at 760 mm., contg. 87 wt. %  $\bar{C}$ . —  $\bar{C}$  + methyl acetate (1:3005):  $\bar{C}$  forms with methyl acetate a const.-boilg. mixt., b.p.  $64.8^\circ$  at 760 mm. (111), contg. 77 wt. %  $\bar{C}$  (111); b.p.  $63.0^\circ$  at 726.3 mm. contg. 50 wt. %  $\bar{C}$  (117); b.p.  $62.6^\circ$  at 717.5 mm. contg. 56 wt. %  $\bar{C}$  (117); for study of constant evapn. system see (125). —  $\bar{C}$  + diisopropyl ether (1:6125):  $\bar{C}$  forms with di-

isopropyl ether a const.-boilg. mixt., b.p.  $66.5^\circ$  at 760 mm. (103). —  $\bar{C}$  + acetone b.p.  $64.3^\circ$  at 760 mm. (109) (103) wt. %  $\bar{C}$  (19) (105), 65.5 mole %  $\bar{C}$  (109); b.p.  $62.4^\circ$  at 732.0 mm. contg. 80 wt. %  $\bar{C}$  (117); b.p.  $62.25^\circ$  at 719 mm. contg. 86 wt. %  $\bar{C}$  (117) cf. also (112); b.p.  $61.95^\circ$  at 716.5 mm. contg. 85 wt. %  $\bar{C}$  (117): for studies of liq.-vapor equil. of  $\bar{C}$  + acetone see (19) (105) (117) (112), for study of vap. press. see (26) (49) (118) (119) (120) (121); for study of distn. of  $\bar{C}$  + acetone in wetted wall column see (122).

TERNARY AZEOTROPES CONTAINING  $\bar{C}$ 

$\bar{C}$  +  $EtOH$  (1:6130) + aq.:  $\bar{C}$  forms with  $EtOH$  + aq. a ternary const.-boilg. mixt., b.p.  $55.4$ – $55.5^\circ$  at 760 mm., contg. about 92.5 wt. %  $\bar{C}$  + 4.0 wt. %  $EtOH$  + 3.5 wt. % aq. (14).



indic. refs. For formn. of  $\bar{C}$  from various chlorinated ketones by action of alkali hypochlorites (haloform reaction) see (235) (236).]

From alcohols. [For concise reviews of prepn. of  $\bar{C}$  from EtOH (1:6130) by action of alkaline hypochlorite solns. see (1) (214); for formn. of  $\bar{C}$  from various other primary and secondary alcohols in similar fashion see (237).]

From miscellaneous sources. [For prepn. of  $\bar{C}$  from trichloroacetic acid (3:1150) by loss of  $CO_2$  under a wide variety of conditions see text of that compound under decarboxylation; from dichloroacetyl chloride (3:5290) on warming with  $AlCl_3$  see text of that compound; from mixtures of salts of fatty acids with inorganic chlorides by electrolysis see (238); from lignin with alkali hypochlorite see (239).]

[For prepn. of trichlorodeuteriomethane (deuteriochloroform) ( $CDCl_3$ ) from chloral deuterate +  $NaOD$  (443) or from chloral (3:5210) +  $D_2O$  +  $CaO$  (444) see indic. refs.; for rate of isotopic exchange between  $\bar{C}$  and  $D_2O$  see (445).]

### CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis of  $\bar{C}$ . [ $\bar{C}$  passed at red heat over asbestos (240), over Pt wire at  $1000^\circ$  (241), with 1%  $I_2$  over pumice at red heat (242) cf. (243), or in electric arc (249) undergoes decomposition, and various proportions of carbon,  $HCl$ , hexachloroethane (3:4835), hexachlorobenzene (3:4939), tetrachloroethylene (3:5460), pentachloroethane (3:6880), and other products are claimed to result.  $\bar{C}$  over htd.  $TiO_2$  gives (245)  $HCl$  +  $CO$  + hexachlorobenzene (3:4939) +  $TiCl_4$ . For other studies of pyrolysis of  $\bar{C}$  at  $368-400^\circ$  (246), at  $425^\circ$  (247), and at  $512^\circ$  (248) see indic. refs.]

Oxidation of  $\bar{C}$ .  $\bar{C}$  is readily oxidized to carbonyl chloride (phosgene) (3:5000) by air, oxygen, ozone, or chemical oxidizing agents. In view of the extremely toxic character of phosgene, and of the extensive use of  $\bar{C}$  in anesthesia, this aspect is of great importance and has been very extensively studied.

By air or oxygen. [For an extensive account of the earlier literature on the oxidation of  $\bar{C}$  in air and light see (250). Note that such oxidation is *not* effected by air in absence of light, nor by light in absence of air (251).  $\bar{C}$  with limited air in sunlight reacts according to the following equation:  $CHCl_3 + O \rightarrow COCl_2$  (3:5000) +  $HCl$  (252) but with excess air in sunlight in sense  $2CHCl_3 + 5O \rightarrow 2CO_2 + 3Cl_2 + H_2O$  (252). Note that  $\bar{C}$  + air over dry  $KOH$  gives (253) some phosgene (3:5000). For later studies on the photochemical oxidation of  $\bar{C}$  (254) in tropical sunlight (255), including search for possible intermediate peroxides (256) (257), see indic. refs. For studies on chlorine-sensitized photochem. oxidn. of  $\bar{C}$  see (258) (259) (260). For oxidn. of  $\bar{C}$  by atomic oxygen see (261). The photochem. oxidn. of  $\bar{C}$  is repressed by various inhibitors of which EtOH has been most extensively studied (262).]

By ozone. [ $\bar{C}$  dissolves ozone yielding a blue soln. in which some  $\bar{C}$  is gradually oxidized (270) (271) to phosgene; for study of  $\bar{C}$  as ozonization solvent see (24) ]

By other chemical means. [ $\bar{C}$  with  $ClSO_3H$  at  $120^\circ$  (263), with  $K_2Cr_2O_7 + H_2SO_4$  (264), or with air over  $CuO$  at  $350-550^\circ$  (265) gives phosgene (3:5000). Note, however, that  $\bar{C}$  with conc.  $H_2SO_4$  above  $200^\circ$  gives (266) (267)  $CO$  +  $CO_2$  +  $HCl$  +  $SO_2$  while  $\bar{C}$  with an equimolal mixt. of  $H_2S_2O_7 + SO_3$  at  $55-60^\circ$  as directed (268) cf. (269) reacts in sense  $CHCl_3 + H_2S_2O_7 + SO_3 \rightarrow CO + 3ClSO_3H$  with  $S_2O_8Cl_2$  (pyrosulfuryl chloride) being formed using more  $SO_3$ , and  $H_2SO_4$  using less  $SO_3$ .]

Inflammability of  $\bar{C}$ . [For studies of inflammability of  $\bar{C}$  in air, oxygen, or  $O_2/N_2O$  mixts. see (272) cf. (273).]

Reduction of  $\bar{C}$ . [ $\bar{C}$  with  $Zn$  + alc.  $HCl$  (274),  $Zn$  +  $AcOH$  (275),  $Zn$  dust + alc.  $NH_3$  (276) (277) (278),  $Al/Hg$  + aq. (275),  $Fe$  +  $AcOH$  (275), or  $Si_3H_8 + AlCl_3$  in abs. of air

(279) gives  $\text{CH}_2\text{Cl}_2$  (3:5020) or further reduction products, e.g.,  $\text{CH}_3\text{Cl}$  (3:7005) or  $\text{CH}_4$  (280);  $\bar{\text{C}}$  with conc.  $\text{HI}$  on htg. gives (281)  $\text{CH}_2\text{I}_2$  [Beil. I-71,  $\text{I}_1$ -(18),  $\text{I}_2$ -(37)];  $\bar{\text{C}}$  with atomic hydrogen gives (282)  $\text{CH}_3\text{Cl}$  (3:7005) +  $\text{HCl}$ .]

**Substitution of  $\bar{\text{C}}$ .** Note that the text of this section refers only to replacement of the single hydrogen atom of  $\text{CHCl}_3$ .

**Fluorination.** [The product of replacement of the H atom of  $\bar{\text{C}}$  by F (289), viz., trichlorofluoromethane,  $\text{CCl}_3\text{F}$  [Beil. I-64], is usually prep'd. by indirect means from sources other than  $\bar{\text{C}}$ , e.g., from  $\text{CCl}_4$  (3:5100) +  $\text{F}_2$  in pres. of As +  $\text{Br}_2$  (283). However, beyond noting a few leading articles on its physical consts., including b.p. =  $23.66^\circ$  (284),  $23.77^\circ$  (285) at 760 mm., m.p. =  $-110.48^\circ$  (284), vapor press (284) (285), liquid density (286), and  $P/V/T$  relationships (287), no complete review of  $\text{CCl}_3\text{F}$  and its relatives (cf. (288)) can be given here.]

**Chlorination.**  $\bar{\text{C}}$  on suitable chlorination yields  $\text{CCl}_4$  (3:5100). [E.g.,  $\bar{\text{C}}$  with  $\text{Cl}_2$  in sunlight (290) or u.v. light (291) (292) (293) (294), at  $260$ – $320^\circ$  (295), or in pres. of  $\text{FeCl}_3$  (296) or of aq. (297), or  $\bar{\text{C}}$  with  $\text{ICl}$  at  $165^\circ$  (298), or  $\bar{\text{C}}$  with aq.  $\text{NaOCl}$  (reaction very slow and incomplete (299)) gives  $\text{CCl}_4$  (3:5100). Note, however, that  $\bar{\text{C}}$  is *not* chlorinated with  $\text{SO}_2\text{Cl}_2$  even in presence of organic peroxides (200).]

**Bromination**  $\bar{\text{C}}$  on suitable bromination gives bromotrichloromethane. [E.g.,  $\bar{\text{C}}$  with  $\text{Br}_2$  in s.t. (301) (298) at  $225$ – $275^\circ$  for 14 hrs. as directed (302), or  $\bar{\text{C}}$  with  $\text{Br}_2$  in light of  $5460 \text{ \AA}$  (303) or  $2650 \text{ \AA}$  in pres. of  $\text{O}_2$  (304), or over carbon at  $180$ – $350^\circ$  (305), or  $\bar{\text{C}}$  with aq.  $\text{NaOBr}$  (299), gives  $\text{CCl}_3\text{Br}$  [Beil. I-67,  $\text{I}_2$ -(31)], b.p.  $105^\circ$  (302),  $104.2$ – $104.35^\circ$  at  $758.5 \text{ mm.}$  (308), m.p.  $-21^\circ$  (302). For prepn. of  $\text{CCl}_3\text{Br}$  from trichloroacetyl bromide by pyrolysis at  $400^\circ$  at ord. press. see (306); for studies of behavior of  $\text{CCl}_3\text{Br}$  with  $\text{Cl}_2$  in light (307) (308) or of its halogen-sensitized photochem. oxidn. (309) see indic. refs.]

**Iodination.** [ $\bar{\text{C}}$  with aq.  $\text{NaOI}$  (299) gives iodotrichloromethane,  $\text{CCl}_3\text{I}$  [Beil. I-71], b.p.  $142^\circ$  (299) (310); for prepn. of this prod. from  $\text{CCl}_4$  (3:5100) with  $\text{AlI}_3$  in  $\text{CS}_2$  (310) or from trichloroacetyl iodide by distn. at ord. press. (306) see indic. refs.]

**Nitration.** [ $\bar{\text{C}}$  with  $\text{HNO}_3$  in s.t. nt  $90$ – $100^\circ$  for 120 hrs. (311) or in boilg. acetyl nitrate (312) gives nitrotrichloromethane (chloropicrin) [Beil. I-76,  $\text{I}_1$ -(20),  $\text{I}_2$ -(41)], b.p.  $111$ – $112^\circ$ , but this product is usually prep'd. by other means, e.g., from calcium picrate with  $\text{Ca}(\text{OCl})_2$  (313) (314).]

**Nitrosation** [No record can be found of any reaction between chloroform and nitrous acid. However, nitrosotrichloromethane [Beil.  $\text{I}_2$ -(39)] has been obtd. indirectly from sodium trichloromethane sulfinate,  $\text{CCl}_3\text{SOONa}$ , by the action of  $\text{HNO}_3$  (315) (316). It is a dark blue liq., b.p.  $5.0$ – $5.5^\circ$  at  $70 \text{ mm}$  (315), but decomposing on distn. at ord. press. The compound is of considerable interest because on reduction with  $\text{H}_2\text{S}$  (315),  $\text{Al/Hg}$  (315),  $\text{SnCl}_2$  (316), or  $\text{SO}_2$  (316) it yields dichloroformaldoxime,  $\text{Cl}_2\text{C}=\text{NOH}$ , a chemical warfare agent with especially terrifying characteristics.]

**Hydrolysis of  $\bar{\text{C}}$ .**  $\bar{\text{C}}$  on hydrolysis gives formic acid (1:1005) in such a form that the reaction mixt. is able to reduce Fehling soln. or  $\text{NH}_4\text{OH}/\text{AgNO}_3$  even at room temp. or more rapidly on warming (dif. from  $\text{CCl}_4$  (3:5100), 1,2-dichloroethane (3:5130), 1,1,2,2-tetrachloroethane (3:5750) and hexachloroethane (3:4835)). Note that, although some CO has been detected, yet formaldehyde (1:0145) is *not* produced (317).

[ $\bar{\text{C}}$  with aq. on protracted htg. in s.t. at  $225^\circ$  gives (318)  $\text{HCOOH}$  (1:1005) +  $\text{CO}$  +

[ $\bar{\text{C}}$  is also hydrolyzed in alc. alk. solns. even more readily than  $\text{CCl}_4$  (3:5100) (321) (191); for use of this principle in estimation of  $\bar{\text{C}}$  see above under determination of  $\bar{\text{C}}$ . For study of kinetics of hydrolysis of  $\bar{\text{C}}$  with alc.  $\text{KOH}$  (325), with  $N/10 \text{ KOH}$  in 95% alc. at  $90^\circ$

(326) cf. (327), or with  $\text{Ba}(\text{OH})_2$  or  $\text{TIOH}$  in 50% alc. (328) (327) see iadic. refs. Note that  $\bar{\text{C}}$  with alc.  $\text{KOH}$  is also claimed by one worker (253) to give ethylene.]

[For further details on ability of  $\bar{\text{C}}$  to reduce Fehling soln. see (317) (329) (330).]

Behavior of  $\bar{\text{C}}$  with inorganic salts. [ $\bar{\text{C}}$  with  $\text{AlCl}_3$  gives a gummy hygroscopic addn prod. which with aq. regenerates  $\bar{\text{C}}$  (331), but  $\bar{\text{C}}$  with  $\text{AlBr}_3$  is more or less (yields: 58-90% (332), 100% (333)) converted to chromoform [Beil. I-68, I<sub>1</sub>-(16), I<sub>2</sub>-(33)], h.p. 149.55° at 760 mm. (334), m.p. 8.05° (334),  $D_4^{25} = 2.87757$  (334),  $D_4^{20} = 2.89054$  (334),  $D_4^{15} = 2.90350$  (334),  $n_D^{15} = 1.60088$  (334).]

[ $\bar{\text{C}}$  with  $\text{CaI}_2$  in s.t. at 100° is partially converted (335) to  $\text{CHI}_3$ , but  $\bar{\text{C}}$  with aq.  $\text{KI}$  even in pres. of  $\text{Cu}$  decomposes yielding (336)  $\text{CH}_4 + \text{H}_2 + \text{CO} + \text{CO}_2$ .]

[For leading reference on behavior of  $\bar{\text{C}}$  with various metal fluorides see (337).]

Behavior of  $\bar{\text{C}}$  with metals. [ $\bar{\text{C}}$  with alkali or even alkaline-earth metals undergoes explosive decompn. on htg. or even at room temp. if subjected to sufficient mechanical shock. For studies of the explosion of  $\bar{\text{C}}$  with alkali metals see (338) (339) (340); for further data on explosions of  $\bar{\text{C}}$  with  $\text{Li}$ ,  $\text{Na}$ ,  $\text{K}$ ,  $\text{Ca}$ ,  $\text{Sr}$ ,  $\text{Ba}$ , and  $\text{Mg}$ , especially with reference to sensitivity to mechanical shock, see (341).  $\bar{\text{C}}$  with molten  $\text{Na}$  at 260-370° as directed (342) gives  $\bar{\text{C}} + \text{H}_2 + \text{CH}_4$  with smaller amts. of  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_2$ ; for study of  $\bar{\text{C}}$  with  $\text{Na}$  vapor see (343).]

[For study of hazards of behavior of  $\text{CHCl}_3/\text{CCl}_4$  mixts. with  $\text{Al}$  or  $\text{Mg}$  see (344); for extensive study of corrosion of metals by  $\bar{\text{C}}$  see (345).]

[Note that  $\bar{\text{C}}$  with  $\text{Mg}$  in hollg. ether does *not* react, even in pres. of various catalysts (346).]

Behavior of  $\bar{\text{C}}$  with various organic reactants. *With carbon monoxide.* [ $\bar{\text{C}}$  with  $\text{CO} +$  water vapor above 200° in pres. of suitable cat. as directed is claimed (347) to give acetic acid (1:1010);  $\bar{\text{C}}$  with  $\text{CO} + \text{AlCl}_3$  at 150° and 900 atm. for 6 hrs. gives (21% yield (348)) dichloroacetyl chloride (3:5290).]

*With hydrocarbons.* [ $\bar{\text{C}}$  (excess) with octene-1 (1:8375) in pres. of small amts. (0.02 mole) of dihenzoyl peroxide (or diacetyl peroxide) adds to unsatd. linkage giving (349) 1,1,1-trichlorooctane; under similar conditions  $\bar{\text{C}}$  adds to one of the unsatd. linkages of diallyl (1:8045) giving 8,8,8-trichloroheptene-1. — (For other addns. of  $\bar{\text{C}}$  to unsatd. linkages see below).]

[ $\bar{\text{C}}$  with  $\text{C}_6\text{H}_6$  (excess) in pres. of  $\text{AlCl}_3$  (350) (351) (352) (353),  $\text{FeCl}_3$  (354), chromium powder (355), or  $\text{Al}$  powder (356) gives triphenylmethane (1:7220); other aromatic hydrocarbons presumably give analogous results but cannot be detailed here.]

*With saturated halohydrocarbons.* [ $\bar{\text{C}}$  (1.2 moles) with  $\text{EtBr}$  (3.8 moles) +  $\text{AlCl}_3$  (0.07 mole) on htg. as directed (357) gives  $\text{EtCl}$  (3:7015) + 90% yield  $\text{CHBr}_3$  (for physical constants see above under behavior of  $\bar{\text{C}}$  with inorganic salts ( $\text{AlBr}_3$ )). —  $\bar{\text{C}}$  (1 mole) with  $\text{MeI}$  (3 moles) +  $\text{AlCl}_3$  (0.04 mole) on similar treatment gives  $\text{MeCl}$  (3:7005) + (95% yield (357)) iodoform, m.p. 119°. —  $\bar{\text{C}}$  with  $\text{CHBr}_3$  + 5-10%  $\text{KCl}$  in pres. of moistened  $\text{AlCl}_3$  under  $\text{CO}_2$  in s.t. at 135° for 14 hrs. undergoes a redistribution reaction giving (358) 17%  $\bar{\text{C}}$  + 43%  $\text{CHCl}_2\text{Br}$  + 31%  $\text{CHClBr}_2$  + 9%  $\text{CHBr}_3$ .]

*With unsaturated halohydrocarbons.* [ $\bar{\text{C}}$  (3 wt. pts.) with ord. 1,2-dichloroethylene (3:5030) +  $\text{AlCl}_3$  (0.25 wt. pt.) stirred with sand for 20 hrs. at 30° (359) cf. (360) (361) (362) gives (yields: 63% (359), 70-75% at 50° (360), 46% at 17° in 22 hrs. (360)) 1,1,2,3,3-pentachloropropane (3:6280).]

[ $\bar{\text{C}}$  with 1,1,2-trichloroethylene (3:5170) +  $\text{AlCl}_3$  at 20° gives (361) (362) 1,1,1,2,3,3-hexachloropropane (3:6460); note that at higher temp., e.g., 50-60°, yield is greatly diminished and several other prods. (361) are formed.]

[ $\bar{\text{C}}$  (2 moles) with 1,1,2,2-tetrachloroethylene (3:5460) +  $\text{AlCl}_3$  (0.2 mole) refluxed 15-20 hrs. gives (85-93% yield (363)) (364) (365) (366) (367) (368) (369) 1,1,1,2,2,3,3-

heptachloropropane (3:0200); for study of equil. of system  $\bar{C}$  + tetrachloroethylene (3:5400) + unsym.-heptachloropropane (3:0200) see [370].]

*With unsaturated nitriles.* [ $\bar{C}$  with acrylonitrile (vinyl cyanide) in pres. of trimethylbenzyl-ammonium hydroxide at 0-5° for 24 hrs or solid KOH at 0-5° for 4 hrs. adds to unsatd. linkage giving (11-12% yield [371]) [372]  $\gamma,\gamma,\gamma$ -trichloro-*n*-butyronitrile, m.p. 41°, b.p. 214-216° at 760 mm, 90-95° at 12 mm [371] [372].]

*With alcohols or alcoholates.* [ $\bar{C}$  with MeOH over cat. at 200-350° gives [373] MeCl (3:7005),  $\bar{C}$  with EtOH under similar conditions gives [373] EtCl (3:7015).]

[ $\bar{C}$  with Na alcoholates gives the corresp. trialkyl orthoformates. E.g.,  $\bar{C}$  with NaOCH<sub>3</sub> gives [374] [375] trimethyl orthoformate (1:3087);  $\bar{C}$  with NaOC<sub>2</sub>H<sub>5</sub> gives (27-31% yield [376], 36% [377]) [374] [375] triethyl orthoformate (1:3241); orthoformate esters of higher alcs are similarly prepd cf [374] [377]. For study of behavior of  $\bar{C}$  with mixts. of sodium alcoholates see [378]; for treatise on chemistry of aliphatic orthoesters see [379].]

*With mercaptans or mercaptides* [ $\bar{C}$  with NaSCH<sub>3</sub> should yield trimethyl trithioorthoformate [Beil. II-(39)], m.p. 16° [380], b.p. 220° dec [380], 103-104° at 12 mm [381], 96° at 9 mm. [380],  $n_D^{25} = 1.5696$  [381], but this prod. has been reported only by other means, e.g., from CCl<sub>4</sub> (3:5100) with NaSCH<sub>3</sub> [381] and from anhydrous HCOOH (1:1005) with CH<sub>3</sub>SH in s.t. at ord. temp. [380].]

[ $\bar{C}$  with NaSC<sub>2</sub>H<sub>5</sub> gives [382] [383] [386] triethyl trithioorthoformate [Beil. II-95, II-(39)], b.p. 235° dec [380], 174° at 760 mm [384], 136.5° at 23 mm. [385], 133° at 21 mm. [380], 120.5-125° at 12 mm. [381], 127-128° cor. at 12 mm [387],  $D_4^{20} = 1.053$  [380],  $n_D^{25} = 1.5410$  [381], but this product is usually prepd by indirect means, e.g., from anhydrous HCOOH (1:1005) with C<sub>2</sub>H<sub>5</sub>SH in pres. of dry HCl [384] [385] or from CCl<sub>4</sub> (3:5100) with NaSC<sub>2</sub>H<sub>5</sub> [381].]

*With phenols or phenolates*  $\bar{C}$  with phenols (or with substituted phenols having at least one free ortho or para position) in presence of aq. alk. condenses with eventual introduction of the formyl radical and forma. of phenolic aldehydes (Reimer-Tiemann reaction [388]). The countless recorded examples of this reaction cannot be detailed here but the following leading references will be found useful. [For modern studies of the Reimer-Tiemann reaction see [389] [390]; for studies of influence of substituents in the phenolic component see [391] [392] [393] [394] [395]; for extension of the Reimer-Tiemann reaction to other classes such as substituted indoles [396], thiazoles [397] see indic. refs.; for application to  $\beta$ -naphthol (1:1540) giving (38-48% yield [398]) 2-hydroxy-1-naphthaldehyde, m.p. 79-80°, to  $\beta$ -tetralol (5,6,7,8-tetrahydronaphthol-2) [399] see indic. refs.; for studies on theory of Reimer-Tiemann reaction see [400] [401] [402].]

[ $\bar{C}$  with dry KOC<sub>6</sub>H<sub>5</sub> at 110° for 4 hrs. under N<sub>2</sub> gives (15% yield [403]) triphenyl orthoformate [Beil. VI-162, VI-(153)], ndls. from alc., m.p. 76-77° [404], 75° [403], 71.5° [405]; note that this prod. is also formed [405] in the Reimer-Tiemann reaction cf. [390].]

*With aldehydes or ketones.*  $\bar{C}$  with aromatic (but not aliphatic [406]) aldehydes of aq. KOH undergoes addition yielding trichloromethyl-aryl-carbinols. benzaldehyde (1:0185) + aq. KOH gives (16% yield [407]) trichloromethyl-phenyl-carbinol [Beil. VI-476, VI-(237)], m.p. 115° [408], b.p. 115° at 15 mm. [409] cf. [406] (corresp. acetate, m.p. 57° [410]) [409] cf. [406] (corresp. acetate, m.p. 97.5° [409]); analogous behavior of  $\bar{C}$  + alkali with *o*-chlorobenzaldehyde (3:6410) [411], *m*-chlorobenzaldehyde (3:6475) [412], *p*-chlorobenzaldehyde (3:0765) [413], *p*-tolualdehyde (1:0215) [412], and furfural (1:0185) [406] see indic. refs. Note that trichloromethyl-aryl-carbinols are also obtd by reaction of arom. hydrocarbons with chloral (3:5210) q.v.]

[ $\bar{C}$  with acetone (1:5400) in pres. of dry powdered KOH (0.5 mole) below 0° [414] or 2-3° [415], or KOH in alc. as directed [416], or even NaNH<sub>2</sub> [418] gives (yields: 25% [416],

23% (414) (417) (415) 1,1,1-trichloro-2-methylpropanol-2 ( $\beta,\beta,\beta$ -trichloro-*tert*-butyl alcohol = "Chloretone") (3:2662) q.v.; note that use of NaOH lowers the yield (414) and that  $\text{Ca}(\text{OH})_2$  (416),  $\text{Zn}(\text{OH})_2$  (414), or  $\text{Al}(\text{OH})_3$  (414) yields no such product; note also that the crude prod. contains some diacetone alcohol (1:6423) best removed by treatment with aq. (416) since otherwise it forms with the "Chloretone" a const.-boilg. mixt.]

$\bar{\text{C}}$  (2 moles) with ethyl methyl ketone (1:5405) in pres. of dry powdered KOH (419) or of  $\text{NaNH}_2$  (418) gives (13.5% yield (419)) by addition 1,1,1-trichloro-2-methylbutanol-2 [Beil. I- (424)], b.p. 162-165° (418), 110-113° dec. at 620 mm. (419),  $D_4^{20} = 1.2128$  (419),  $n_D^{20} = 1.4460$  (419). Note, however, that analogous addition of  $\bar{\text{C}}$  does not occur with diethyl ketone (1:5420) (420), di-*n*-propyl ketone (1:5447) (420), ethyl *n*-propyl ketone (420), methyl isobutyl ketone (1:5430) (420), or methyl phenyl ketone (acetophenone) (1:5515) (419), but will occur to a very small extent with cyclopentanone (1:5446) (421) or cyclohexanone (1:5465) (421) cf. (418).]

With amines.  $\bar{\text{C}}$  with primary amines in pres. of alc. caustic alkali condenses with loss of 3 HCl giving the corresp. isocyanides whose extremely characteristic odor has caused this general procedure to be used as a test (422) for primary amines. The reaction has, however, been very little studied in the aliphatic series.

$\bar{\text{C}}$  with  $\text{CH}_3\text{NH}_2$  + alc. NaOH should give methyl isocyanide (methyl carbylamine) [Beil. IV-56, IV- (328), IV- (561)], b.p. 59.6° at 760 mm. (423), 59-60° (424),  $D_4^{20} = 0.734$  (424),  $D_4^{20} = 0.7464$  (425),  $n_D^{20} = 1.343$  (424), but this highly explosive (425) (426) (427) substance has been reported only by other means, e.g., from MeI with dry AgCN (425) (423), CuCN (428), or  $\text{CH}_3\text{HgI}$  (429). —  $\bar{\text{C}}$  with  $\text{C}_2\text{H}_5\text{NH}_2$  + alc. NaOH gives (430) ethyl isocyanide (ethyl carbylamine) [Beil. IV-107, IV- (351), IV- (600)], b.p. 78.1° at 760 mm. (431), 78° (424),  $D_4^{20} = 0.747$  (424),  $D_4^{20} = 0.7405$  (425),  $n_D^{20} = 1.362$  (424), but this less explosive prod. (427) is usually obtd. by other means, e.g., from EtI with AgCN (425) (431), etc. —  $\bar{\text{C}}$  with *n*-BuNH<sub>2</sub> + aq. NaOH gives (only 5% yield (432)) *n*-butyl isocyanide (*n*-butyl carbylamine) which is better obtd. (40% yield (432)) from *n*-BuI + AgCN.]

$\bar{\text{C}}$  with aniline in alc. KOH (433) (435) cf. (438) or in  $\text{C}_6\text{H}_6$  +  $\text{NaNH}_2$  (436), or better in MeOH/NaOH (50% yield (434)) or powdered KOH without solvent (35-40% yield (437)) cf. (438), gives phenyl isocyanide (phenyl carbylamine) [Beil. XII-191, XII- (168)], b.p. 165-166° at ord. press. with partial polymerization (435), 78° at 40 mm. (435), 64° at 20 mm. (435),  $D_4^{25.1} = 0.9823$  (424),  $n_D^{25.1} = 1.52828$  (424). — For analogous reactions of  $\bar{\text{C}}$  with *o*-toluidine giving *o*-tolyl isocyanide [Beil. XII-788], b.p. 183-184° cor. at 753 mm. (439), with *p*-toluidine giving (440) (441) *p*-tolyl isocyanide [Beil. XII-903], b.p. 99° at 32 mm. (441), 94° at 25 mm. (434), m.p. 21° (441), 19.5° (434), with *p*-methoxyaniline (*p*-anisidine) giving *p*-methoxyphenyl isocyanide, m.p. 33° (438), 30° (434), with *o*-methoxyaniline (*o*-anisidine) giving *o*-methoxyphenyl isocyanide, b.p. 112° at 16 mm. (438), with *p*-phenylenediamine to give (442) either *p*-aminophenyl isocyanide, m.p. 74°, or *p*-phenylene diisocyanide see indic. refs. — Many other isocyanides are known but cannot be detailed here.]

Ⓐ Color reaction with  $\alpha$ -naphthol/cyclohexanol. A.  $\bar{\text{C}}$  (1 drop) with 2 ml. of a 2% soln. of  $\alpha$ -naphthol (1:1500) in cyclohexanol (1:6415) + 1 pellet of solid NaOH, boiled 25 seconds and cooled, gives (174) blue color; one portion of this blue soln. underlaid with equal vol. of 85%  $\text{H}_2\text{SO}_4$ , stood 1 minute and shaken turns intensely blue; a second portion of the alkaline blue soln. acidified with equal vol. of AcOH (1:1010) stood 1 minute and shaken becomes orange-yellow. [Note that the alkaline boiling also gives a blue color with  $\text{CH}_2\text{Cl}_2$  (3:5020) and with  $\text{CCl}_4$  (3:5100) while other chlorinated solvents (174) give yellow-brown, gray, or brown; in the  $\text{H}_2\text{SO}_4$  treatment  $\text{CH}_2\text{Cl}_2$  (3:5020) gives greenish-blue and  $\text{CCl}_4$  (3:5100) an intense blue; in the AcOH treatment  $\text{CH}_2\text{Cl}_2$  (3:5020) gives a yellow,  $\text{CCl}_4$  (3:5100) a red, color.]

B.  $\bar{C}$  (1 drop) with 2 ml. cyclohexanol (1:6415) + a few mgms.  $\alpha$ -naphthol (1:1500) + 2 ml. 20% aq. KOH boiled 15 seconds with vigorous shaking gives (175) blue color in upper layer. [Neither  $CH_2Cl_2$  (3:5020) nor  $CCl_4$  (3:5100) gives any color, and this form of the test may be used to detect as little as 1%  $\bar{C}$  in either of the other two.]

Ⓔ Color test with 2,7-dihydroxynaphthalene/cyclohexanol.  $\bar{C}$  (1 drop) with 2 ml. pure cyclohexanol (1:6415) + 1 pellet NaOH + a few mgms. 2,7-dihydroxynaphthalene htd. at 197° (b.p. of ethylene glycol) for 45 seconds, decanted from undissolved NaOH, cooled, and shaken with 2 ml. AcOH + 4 ml. 96% EtOH, gives deep red color (175). [Note that under these conditions  $CH_2Cl_2$  (3:5020) gives a steel-blue color while  $CCl_4$  (3:5100) gives pale yellow-brown color (175).]

Ⓕ Color test with cyclopentanol.  $\bar{C}$  (1 drop) in 1 ml. cyclopentanol (1:6412) + 1 pellet NaOH boiled for 25 seconds, then shaken vigorously for 35 seconds, then treated with 4 ml. 96% EtOH and shaken, gives with  $\bar{C}$  only a pale citron-yellow color (175). [Note that in this test  $CH_2Cl_2$  (3:5020) gives a deep red color which intensifies or turns reddish-brown upon addition of EtOH;  $CCl_4$  (3:5100) gives an intense brown color.]

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## 3:5060 OXALYL (DI)CHLORIDE



Beil. II - 542

II<sub>1</sub>-(234)II<sub>2</sub>-(608)

B.P.

M.P.

03.5-64° at 763 mm. (1)

-10.0° (3)

D<sub>4</sub><sup>20</sup> = 1.4785 (3)n<sub>D</sub><sup>20</sup> = 1.4316 (3)

02.1-62.3° (2)

-12.0° (1)

1.480 (4)

1.4301 (4)

61.1° at 743 mm. (3)

D<sub>4</sub><sup>13.4</sup> = 1.4484 (4)

00-01° (4)

D<sub>4</sub><sup>12.9</sup> = 1.4888 (4)

50-60° (5)

n<sub>D</sub><sup>12.9</sup> = 1.43445 (4)

1.43305 (4)

[See also ethoxalyl chloride (3:5025).]

Colorless liq. whose vapors strongly attack respiratory passages. — Solns. of C in ether, CHCl<sub>3</sub>, or alkanes are colorless, but those in phenol, anisole, thioethers, piperonal, and dipentene are yellow (5). — Note that the presence in samples of C of phosphorous compts.

(such as might remain from the reagents used in its prepn.) increases the refractive index (4); such contaminants may be removed by treatment with  $\text{Cl}_2$  and subsequent fractionation (4) (7). —  $\bar{\text{C}}$  is stable to fuming  $\text{H}_2\text{SO}_4$ .

$\bar{\text{C}}$  is an important reagent in organic synthesis; its reactions may conveniently be classified under four main types, viz.: (A) those in which it reacts as an acid chloride (either one or both groups being involved); (B) those in which it acts like a mixture of  $\text{COCl}_2$  (3:5000) +  $\text{CO}$ ; (C) those in which it acts as a chlorinating agent; and (D) those in which it acts as a dehydrating agent. Examples of all these types will be found in the subsequent text, but naturally combinations of the distinctive types may occur simultaneously.

$\bar{\text{C}}$  is also employed in the preparation of various dyestuffs although these cannot be discussed here. [For toxicity of  $\bar{\text{C}}$  see (6); for protection of stopcocks from action of  $\bar{\text{C}}$  see (16).]

**Preparation.** [For prepn. of  $\bar{\text{C}}$  from anhydrous oxalic acid (1:0535) with  $\text{PCl}_5$  (2 moles) (yields: 70% (8), 45–50% (1)) in pres. of an inert solid or liq. diluent (9) and even in units as much as 5 times the original (10), or with  $\text{PCl}_3$  in  $\text{POCl}_3$  in stream of  $\text{Cl}_2$  (11), or with  $\text{COCl}_2$  (3:5000) in pres. of tertiary amines (14) see inde. refs.; from diethyl oxalate (1:1055) with  $\text{PCl}_5$  (poor yields) see (12) (1) (13).]

[For prepn. of  $\bar{\text{C}}$  from  $\text{COCl}_2$  (3:5000) +  $\text{CO}$ , or from  $\text{CO}$  +  $\text{Cl}_2$  over suitable cat. at 200–400° and 200 atm. press., see (15) ]

[For formn. of  $\bar{\text{C}}$  (19% yield (1)) from ethoxalyl chloride (3:5625) with  $\text{PCl}_5$  in s.t. at 170° see (1) ]

**Pyrolysis or decomposition of  $\bar{\text{C}}$ .** [ $\bar{\text{C}}$  on passing through tube at 600° (1) or on htg. at 340° for 70 hrs. in an evacuated s.t. (7) dec. quant. into  $\text{COCl}_2$  (3:5000) and  $\text{CO}$ ; note, however, that at 200°  $\bar{\text{C}}$  shows no trace of phosgene even after 18 hrs. (7) and at ordinary temp. (when protected from light and moisture) can be preserved indefinitely.]

$\bar{\text{C}}$  (1 mole) on slight warming with  $\text{AlCl}_3$  (2 moles) in  $\text{CS}_2$  dec. quant. (1) into phosgene (3:5000) +  $\text{CO}$  and may thus serve as a source of  $\text{COCl}_2$  in Friedel-Crafts reactns. (see below).

$\bar{\text{C}}$  when exposed to light of any wave length below 3800 Å slowly dec., the final prods. being  $\text{COCl}_2$  (3:5000) +  $\text{CO}$  although the initial prods. appear to include  $\text{Cl}_2$  and  $\text{CO}$  (16); this photochemical decn. plays an important part in its use as a reagent for introduction of the  $-\text{COCl}$  group (chloroformylation) (see below).

**Behavior of  $\bar{\text{C}}$  with inorganic reactants.**  $\bar{\text{C}}$  with liq. aq. or dil. aq. alk. yields quant. (1)  $\text{CO}$  +  $\text{CO}_2$  +  $\text{HCl}$ , no trace of oxalic acid (1:0445) or of its semi-acid chloride being formed; however,  $\bar{\text{C}}$  as vapor on treatment with steam does yield also some oxalic acid crystals (1).

$\bar{\text{C}}$  in ether on treatment with dry  $\text{H}_2\text{S}$  for several hrs. is unchanged, but if quinoline (2 moles) is added, vigorous reactn. occurs (1) with evolution of gaseous  $\text{CO}$  +  $\text{COS}$ .]

$\bar{\text{C}}$  on treatment with  $\text{HBr}$  gas for 12 hrs. gives (85% yield (7)) (17) (18) oxalyl (di)bromide [Beil.  $\text{II}_1$ -(236),  $\text{II}_2$ -(509)], b.p. 106° (18), 102–103° at 720 mm., 16–17° at 10 mm., f.p. –19.5° (7) (for study of thermal and photochemical decn. of this prod. see (18)). —  $\bar{\text{C}}$  with  $\text{HI}$  is reduced (7) yielding  $\text{CO}$  +  $\text{I}_2$  (cf. phosgene (3:5000)).]

$\bar{\text{C}}$  with 2  $\text{NaI}$  in dry acetone yields quant. (41)  $\text{CO}$  +  $\text{I}_2$  + 2 $\text{NaCl}$  but  $\bar{\text{C}}$  with aq.  $\text{NaI}$  does not set free iodine giving instead the usual aqueous hydrolysis with formn. of  $\text{CO}$  +  $\text{CO}_2$  + 2 $\text{HCl}$  (41).

$\bar{\text{C}}$  (2 moles) with  $\text{As}_2\text{O}_3$  (1 mole) gives (95% yield (19))  $\text{AsCl}_3$ , b.p. 130°; similarly  $\bar{\text{C}}$  with dry  $\text{CrO}_3$  refluxed 5 hrs. gives (80% yield (19)) chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , b.p. 114–116° at 745 mm.]

$\bar{\text{C}}$  in  $\text{C}_6\text{H}_6$  with  $\text{H}_2$  in pres. of  $\text{Pd/BaSO}_4$  cat. gives only gaseous products, no trace of glyoxal or glyoxylic acid being formed (20).]

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## 3:5060 OXALYL (DI)CHLORIDE



Bell. II - 542

II<sub>1</sub>-(231)II<sub>2</sub>-(508)

B.P.

M.P.

63.5-64° at 763 mm. (1)

-10.0° (3)

D<sub>4</sub><sup>20</sup> = 1.4785 (3) n<sub>D</sub><sup>20</sup> = 1.4316 (3)

62.1-62.3° (2)

-12.0° (1)

1.480 (4) 1.4301 (4)

61.1° at 743 mm. (3)

D<sub>4</sub><sup>13.4</sup> = 1.4484 (4)

60-61° (4)

D<sub>4</sub><sup>12.0</sup> = 1.4888 (4) n<sub>D</sub><sup>12.0</sup> = 1.43145 (4)

59-60° (5)

1.43395 (4)

[See also ethoxalyl chloride (3:5625).]

Colorless liq. whose vapors strongly attack respiratory passages. — Solns. of  $\bar{\text{C}}$  in ether, CHCl<sub>3</sub>, or alkanes are colorless, but those in phenol, anisole, thioethers, piperonal, and dipentene are yellow (5). — Note that the presence in samples of  $\bar{\text{C}}$  of phosphorous compds.

(such as might remain from the reagents used in its preparation) increases the refractive index (4); such contaminants may be removed by treatment with  $\text{Cl}_2$  and subsequent fractionation (4) (7). —  $\bar{\text{C}}$  is stable to fuming  $\text{H}_2\text{SO}_4$ .

$\bar{\text{C}}$  is an important reagent in organic synthesis; its reactions may conveniently be classified under four main types, viz.: (A) those in which it reacts as an acid chloride (either one or both groups being involved); (B) those in which it acts like a mixture of  $\text{COCl}_2$  (3:5000) + CO; (C) those in which it acts as a chlorinating agent; and (D) those in which it acts as a dehydrating agent. Examples of all these types will be found in the subsequent text, but naturally combinations of the distinctive types may occur simultaneously.

$\bar{\text{C}}$  is also employed in the preparation of various dyestuffs although these cannot be discussed here. [For toxicity of  $\bar{\text{C}}$  see (5); for protection of stopcocks from action of  $\bar{\text{C}}$  see (16).]

Preparation. [For prepn. of  $\bar{\text{C}}$  from anhydrous oxalic acid (1:0535) with  $\text{PCl}_5$  (2 moles) (yields 70% (8), 45–50% (1)) in pres. of an inert solid or liq. diluent (9) and even in units as much as 5 times the original (10), or with  $\text{PCl}_5$  in  $\text{POCl}_3$  in stream of  $\text{Cl}_2$  (11), or with  $\text{COCl}_2$  (3:5000) in pres. of tertiary amines (14) see indic. refs.; from diethyl oxalate (1:1055) with  $\text{PCl}_5$  (poor yields) see (12) (1) (13).]

[For prepn. of  $\bar{\text{C}}$  from  $\text{COCl}_2$  (3:5000) + CO, or from CO +  $\text{Cl}_2$  over suitable cat. at 200–400° and 200 atm. press., see (15).]

[For formn. of  $\bar{\text{C}}$  (19% yield (1)) from ethoxalyl chloride (3:5625) with  $\text{PCl}_5$  in s.t. at 170° see (1).]

Pyrolysis or decomposition of  $\bar{\text{C}}$ . [ $\bar{\text{C}}$  on passing through tube at 600° (1) or on h.t. at 340° for 70 hrs. in an evacuated s.t. (7) dec. quant. into  $\text{COCl}_2$  (3:5000) and CO; note, however, that at 200°  $\bar{\text{C}}$  shows no trace of phosgene even after 18 hrs. (7) and at ordinary temp. (when protected from light and moisture) can be preserved indefinitely.]

$\bar{\text{C}}$  (1 mole) on slight warming with  $\text{AlCl}_3$  (2 moles) in  $\text{CS}_2$  dec. quant. (1) into phosgene (3:5000) + CO and may thus serve as a source of  $\text{COCl}_2$  in Friedel-Crafts reactns. (see below).

$\bar{\text{C}}$  when exposed to light of any wave length below 3500 Å slowly dec., the final prods. being  $\text{COCl}_2$  (3:5000) + CO although the initial prods. appear to include  $\text{Cl}_2$  and CO (16); this photochemical decn. plays an important part in its use as a reagent for introduction of the —CO.Cl group (chloroformylation) (see below).

Behavior of  $\bar{\text{C}}$  with inorganic reactants.  $\bar{\text{C}}$  with liq. aq. or dil. aq. alk. yields quant. (1) CO +  $\text{CO}_2$  + HCl, no trace of oxalic acid (1:0445) or of its semi-acid chloride being formed; however,  $\bar{\text{C}}$  as vapor on treatment with steam does yield also some oxalic acid crystals (1).

[ $\bar{\text{C}}$  in ether on treatment with dry  $\text{H}_2\text{S}$  for several hrs. is unchanged, but if quinoline (2 moles) is added, vigorous reactn. occurs (1) with evolution of gaseous CO + COS.]

[ $\bar{\text{C}}$  on treatment with HBr gas for 12 hrs. gives (85% yield (7)) (17) (18) oxalyl (di)bromide [Beil. II<sub>1</sub>-(236), II<sub>2</sub>-(509)], b.p. 106° (18), 102–103° at 720 mm., 16–17° at 10 mm., f.p. –19.5° (7) (for study of thermal and photochemical decn. of this prod. see (18)). —  $\bar{\text{C}}$  with  $\text{HI}$  is reduced (7) yielding CO +  $\text{I}_2$  (cf. phosgene (3:5000)).]

$\bar{\text{C}}$  with 2 NaI in dry acetone yields quant. (41) CO +  $\text{I}_2$  + 2NaCl but  $\bar{\text{C}}$  with aq. NaI does not set free iodine giving instead the usual aqueous hydrolysis with formn. of CO +  $\text{CO}_2$  + 2HCl (41).

[ $\bar{\text{C}}$  (2 moles) with  $\text{As}_2\text{O}_3$  (1 mole) gives (95% yield (19))  $\text{AsCl}_3$ , b.p. 130°; similarly  $\bar{\text{C}}$  with dry  $\text{CrO}_3$  refluxed 5 hrs. gives (80% yield (19)) chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , b.p. 114–116° at 748 mm.]

[ $\bar{\text{C}}$  in  $\text{C}_6\text{H}_6$  with  $\text{I}_2$  in pres. of Pd/ $\text{BaSO}_4$  cat. gives only gaseous products, no trace of glyoxal or glyoxylic acid being formed (20).]

$\bar{C}$  in  $C_6H_6$  with  $NH_3$  gas in cold reacts vigorously yielding (21) oxalic acid diamide (oxamide) [Beil. II-545, II<sub>1</sub>-(237), II<sub>2</sub>-(509)], m.p. above  $400^\circ$  (and therefore useless as derivative for identification), +  $NH_4Cl$ . —  $\bar{C}$  with hydrazine hydrate (excess) presumably yields oxalic acid dihydrazide ("oxalhydrazide") [Beil. II-559, II<sub>1</sub>-(243), II<sub>2</sub>-(514)], m.p.  $244^\circ$  dec., although this method of prepn. seems to be unreported.

[ $\bar{C}$  with K/Na alloy is (like many halogen compds.) sensitive to detonation by mechanical shock (GREAT DANGER) cf. (22). — For behavior of  $\bar{C}$  with other metals see (7).]

Behavior of  $\bar{C}$  with organic reactants. Reaction of  $\bar{C}$  with alkanes and cycloalkanes. [ $\bar{C}$  with satd. aliphatic hydrocarbons and with cycloparaffins in pres. of light and peroxides reacts to replace 1 H atom by the  $-CO.Cl$  group (22) (10); since this group represents the radical corresponding to the unisolatable acid chloride of formic acid, the process might well be designated as "chloroformylation"; however, since the resultant prodn. may readily be hydrolyzed to the corresp. carboxylic acids, the process has also (unfortunately) been designated as "carboxylation." — E.g.,  $\bar{C}$  (1 mole) with cyclohexane (1:8405) (2 moles) + dibenzoyl peroxide (0.005 mole) refluxed for 24 hrs. in light from low-pressure Hg vapor lamp (10) or 300-watt tungsten lamp (23) gives (yields: 85% (23), 65% (10)) cyclohexanecarboxylic acid chloride (hexahydrobenzoyl chloride) (3:8580). — Note that neither simple olefins such as 2-methylbutene-2 (1:8220), octene-1 (1:8375), hexadecene-1 (octene) (1:7000), nor cycloalkenes such as cyclohexene (1:8070) undergo this type of reactn. (24), although phenylethylene (styrene) (1:7435) gives cinnamoyl chloride (3:0330) (0% yield of cinnamic ac. after hydrolysis (24)) and phenylacetylene (1:7425) gives  $\beta$ -chlorocinnamoyl chloride (16% yield of  $\beta$ -chlorocinnamic acid after hydrolysis (24)). — Note also that  $\bar{C}$  under similar conditions with aralkyl hydrocarbons chloroformylates the side chain but yields are very low (5-10%) (25).]

Reactions of  $\bar{C}$  with aromatic hydrocarbons. [ $\bar{C}$  with aromatic hydrocarbons (R.H.) in pres. of  $AlCl_3$  shows both (A) and (B) types of reactn. mentioned above in 2nd paragraph; on one hand (A)  $\bar{C}$  reacts like phosgene yielding  $R.CO.Cl$  (which during the usual subsequent treatment is hydrolyzed to the corresp. acid) and ketones of the type  $R_2CO$ ; on the other (B)  $\bar{C}$  reacts with 2 PH as a bifunctional acid chloride yielding the corresp. 1,2-diketones, which with some of the polycyclic hydrocarbons comprise new cyclic systems of the quinone type. Examples of these various combinations are listed below.]

[ $\bar{C}$  with  $C_6H_6$  +  $AlCl_3$  in  $CS_2$  gives according to mode of procedure either (1) 100% yield benzoyl chloride (3:6240) or 89% yield diphenyl ketone (benzophenone) (1:5150); note that no benzil (dibenzoyl) (1:9015) is formed here although it has been ohtd. (in small proportion) together with benzophenone from oxalyl (di)bromide with  $C_6H_6$  +  $AlBr_3$  in  $CS_2$  (17). —  $\bar{C}$  with toluene +  $AlCl_3$  in  $CS_2$  gives (65% yield (26)) *p*-toluic acid (1:0795). —  $\bar{C}$  with *o*-xylene (1:7430) +  $AlCl_3$  in  $CS_2$  gives (75-80% yield (27)) (26) 3,4-dimethylbenzoic acid [Beil. IX-535, IX<sub>1</sub>-(210)], m.p.  $166^\circ$ , accompanied by some 3,4,3',4'-tetramethylbenzil (4,4'-*o*-xylid), m.p.  $128.5^\circ$  cor. (27);  $\bar{C}$  with *m*-xylene (1:7420) similarly gives (40-50% yield (26)) 2,4-dimethylbenzoic acid [Beil. IX-531, IX<sub>1</sub>-(209)], m.p.  $126^\circ$ ;  $\bar{C}$  similarly with *p*-xylene (1:7415) gives (100% yield (26)) 2,5-dimethylbenzoic acid [Beil. IX-534, IX<sub>1</sub>-(210)], m.p.  $132^\circ$ . —  $\bar{C}$  with ethylbenzene (1:7410) gives (29) *p*-ethylbenzoic acid [Beil. IX-529], m.p.  $112^\circ$ .]

[ $\bar{C}$  with arom. hydrocarbons contg. two uncondensed benzene nuclei shows a distinct tendency to yield dicarboxylic acids despite the fact that the first member is exceptional. E.g.,  $\bar{C}$  with biphenyl (1:7175) +  $AlCl_3$  in  $CS_2$  gives (30) 40% yield di-*p*-xenylic ketone, m.p.  $236^\circ$ , + 25% *p*-xenylic acid, m.p.  $140-141^\circ$ , although the formation in 75% yield of *p*-phenylbenzoic acid (*p*-xenoic acid) [Beil. IX-671, IX<sub>1</sub>-(280)], m.p.  $224^\circ$ , has also been reported (31); for examples of dicarboxylic acid formn. from  $\bar{C}$  +  $AlCl_3$  with 2,2'-dimethylbiphenyl (26), diphenylmethane (32), phenyl *p*-tolylmethane (26), di-*p*-tolylmethane (26),  $\alpha,\beta$ -

diphenylethane (bihenyl) {32},  $\alpha,\beta$ -diphenylethylene (stilbene) {32}, triphenylmethane {32}, see indic. refs.]

[ $\bar{C}$  with polycyclic arom. hydrocarbons frequently, but not always, also gives polycyclic quinones; e.g.,  $\bar{C}$  with naphthalene (1:7200) +  $AlCl_3$  in  $CS_2$  gives {35} a mixt. of  $\alpha$ -naphthoic acid (1:0785) +  $\beta$ -naphthoic acid (1:0800);  $\bar{C}$  with 2-methylnaphthalene (1:7605) +  $AlCl_3$  in  $CS_2$  gives {33} a mixt. of acids + 2,2'-dimethylnaphthal + 3-methylacenaphthene-quinone-1,2; for analogous results with 1,6-, 2,6-, and 2,7-dimethylnaphthalenes see {33} {34};  $\bar{C}$  with anthracene +  $AlCl_3$  in  $CS_2$  gives (70% yield {35}) aceanthrenequinone (1,9-oxalylanthracene) [Beil. VII<sub>1</sub>-(436)], red pr. from  $C_6H_6$ , m.p. 270°, accompanied by some anthracene-9-carboxylic acid (*meso*-anthroic acid).]

[For behavior of  $\bar{C}$  +  $AlCl_3$  with 2-methylantracene {36} {38}, 1,2-dibenzanthracene {37}, retene or dihydrotene {39}, or fluoranthene {40} see indic. refs.; many analogous cases are known but cannot be included here.]

*Reaction of  $\bar{C}$  with alcohols and thiols.* [ $\bar{C}$  with 2 moles primary alcs. especially in pres. of pyridine yields corresp. neutral esters; e.g.,  $\bar{C}$  with MeOH (1:6120) (2 moles) gives dimethyl oxalate (1.0415), m.p. 54°;  $\bar{C}$  with EtOH (1:6130) (2 moles) gives diethyl oxalate (1.1055), h.p. 185°; for analogous behavior of  $\bar{C}$  with *n*-propyl alc. (1:6150) yielding di-*n*-propyl oxalate (1.3726), with isobutyl alc. (1:6165) yielding di-isobutyl oxalate (1:3897), with isoamyl alc. (1:6200) yielding diisoamyl oxalate (1:4181) all in 100% yield see {42}. —  $\bar{C}$  with secondary alcs. (2 moles) also yields {42} {50} the corresp. neutral esters, but yields are less satisfactory and the ability of  $\bar{C}$  to act as a dehydrating agent begins to become evident {42}; e.g.,  $\bar{C}$  with methyl-phenyl-carbinol (1:6475) yields no ester, but only phenylethylene (styrene) (1:7435). —  $\bar{C}$  with tertiary alcs. replaces OH by Cl; e.g.,  $\bar{C}$  with *ter*-butyl alc. (1:6140) gives *ter*-butyl chloride (3:7015);  $\bar{C}$  with triphenylcarbinol (1:5985) gives chlorotriphenylmethane (3:3410) {42}.]

[Note that  $\bar{C}$  with only 1 mole of primary alcs. yields the corresponding half esterification prods.; e.g.,  $\bar{C}$  (1 mole) with EtOH (1:6130) (1 mole) gives (60% yield {43}) ethoxalyl chloride (3:5625); for other examples together with use of such oxalin ester chlorides in prepn. of cellulose esters see {43}.]

[ $\bar{C}$  with ethylene glycol (1:6165) (1 mole) directly {42} or in pyridine {44} or in dry ether {45} gives (57% yield {45}) monomeric ethylene glycol oxalate (2,3-dioxodioxane-1,4) [Beil. XIX-153, XIX<sub>1</sub>-(679)], m.p. 143° {45}, 149° {44}, 153° {42}; for relationships of this monomer to the polymeric forms see {46}.]

[ $\bar{C}$  with  $CH_3SH$  (2 moles) {13} in dry ether {47} gives dimethyl dithioloxalate [Beil. II-565, II<sub>1</sub>-(514)], yel. cryst. from ether or ligr., m.p. 82.5–83.5° {13}, 80° {47}, h.p. 218° at 760 mm. {47}. —  $\bar{C}$  with  $EtSH$  (2 moles) {13} {48} in dry ether {1} gives diethyldithioloxalate [Beil. II-565, II<sub>1</sub>-(244)], m.p. 27–27.5° {13}, 24–25° {1}, h.p. 238–240° at 757 mm. {1}, 235° {13}.]

*Behavior of  $\bar{C}$  with phenols and thiophenols.* [ $\bar{C}$  (1 mole) with phenol (2 moles) in dry ether with metallic Na (2 moles) gives (21% yield {49}) diphenyl oxalate [Beil. VI-155, VI<sub>1</sub>-(87)], m.p. 131° u.c. {49}. —  $\bar{C}$  (1 mole) with *o*-cresol (1:1400) (2 moles) + Na similarly gives {49} di-*o*-tolyl oxalate [Beil. VI-355], ndls. from alc., m.p. 90–91° u.c. {49};  $\bar{C}$  with *m*-cresol (1:1730) similarly gives {49} di-*m*-tolyl oxalate [Beil. VI-379, VI<sub>1</sub>-(187)], ndls. from alc., m.p. 105° u.c. {49};  $\bar{C}$  with *p*-cresol (1:1410) similarly {49} or in pyridine {51} gives di-*p*-tolyl oxalate [Beil. VI-398, VI<sub>1</sub>-(201)], pl. from alc. + ether, m.p. 148° {49}, 147° {51}, for similar behavior of still other phenols see {51}.]

[Note, however, that  $\bar{C}$  (1 mole) with phenols (1 mole) in pres. of  $AlCl_3$  leads to mono-esterification followed by elimination of HCl and ring closure; e.g.,  $\bar{C}$  (1 mole) with  $\beta$ -naphthol (1:1510) +  $AlCl_3$  in  $CS_2$  gives (85% yield {52} {53}) 4,5-benzocumarandione-2,3 [Beil. XVII<sub>1</sub>-(267)], orange ndls. from AcOH, m.p. 180–181° {52}.]



[For behavior of  $\bar{C}$  with resorcinol (1:1530) + Na or K in moist ether see (54).]

[ $\bar{C}$  with  $\beta$ -thionaphthol (2-mercaptanaphthalene) +  $AlCl_3$  in  $CS_2$  esterifies and ring-closes with loss of HCl yielding (55) 4,5-benzothiocoumarandione-2,3 (4,5-benzothionaphthenequinone-2,3), red pdr., m.p. 153°. — For extension of this type of reactn. to prepn. of halogenated thionaphthisatins from  $\bar{C}$  with halogenated 1- or 2-mercaptanaphthalenes +  $AlCl_3$  see (56+).]

[For behavior of  $\bar{C}$  with dithiopyrocatechol (*o*-dimercaptobenzene) see (57).]

[For study of a series of molecular cpds. of  $\bar{C}$  with various hydroxy-azo compds. see (58).]

*Behavior of  $\bar{C}$  with phenol ethers.* [ $\bar{C}$  with mononuclear phenol ethers +  $AlCl_3$  reacts in general according to types A and B of paragraph 2 (above) so that after aqueous treatment involved in destroying the  $AlCl_3$  there results either a diketone or a carboxylic acid; which of these is formed or their proportion varies with nature of components and with conditions. E.g.,  $\bar{C}$  (1 mole) with anisole (methyl phenyl ether) (1:7445) (2 moles) +  $AlCl_3$  (2 moles) in  $CS_2$  gives (yields: 90% (59), 80% (60), 76% (17)) anisil (4,4'-dimethoxybenzil) [Beil. VIII-428, VIII<sub>1</sub>-(705)], golden-yel. ndls. from alc., m.p. 133° (60), 132° (59);  $\bar{C}$  (1 mole) with phenetole (ethyl phenyl ether) (1:7485) (2 moles) +  $AlCl_3$  in  $CS_2$  gives (80% yield (29)) phenetil (4,4'-diethoxybenzil), pr. from ether + alc., m.p. 149°;  $\bar{C}$  similarly with *o*-cresol methyl ether (1:7480) +  $AlCl_3$  in  $CS_2$  gives (76% yield (61)) (59) 4,4'-dimethoxy-3,3'-dimethylbenzil, pale yel. ndls. from AcOH, toluene, or pyridine, m.p. 177° (61), 174° (59). — Note, however, that  $\bar{C}$  with *m*-cresol methyl ether (1:7510) +  $AlCl_3$  in  $CS_2$  yields no diketone, but only (59) 2-hydroxy-6-methylbenzoic acid (6-methylsalicylic acid) [Beil. X-217, X<sub>1</sub>-(95)], m.p. 168°;  $\bar{C}$  with *p*-cresol methyl ether (1:7495) gives no diketone but only (12% yield (59)) 2-hydroxy-5-methylbenzoic acid (5-methylsalicylic acid) [Beil. X-227, X<sub>1</sub>-(98)], m.p. 149° (59). — Many analogous cases of each type are known but cannot be included here.]

[ $\bar{C}$  with pyrocatechol dimethyl ether (veratrole) (1:7560) +  $AlCl_3$  gives (60) 2,3,2',3'-tetramethoxybenzophenone;  $\bar{C}$  with resorcinol dimethyl ether (1:7570) gives (60) 2,4,2',4'-tetramethoxybenzophenone;  $\bar{C}$  with hydroquinone dimethyl ether (1:7160) gives (60) 2,5,2',5'-tetramethoxybenzophenone, but  $\bar{C}$  with orcinol dimethyl ether (3,5-dimethoxytoluene) +  $AlCl_3$  gives (29) by ring closure 6-methoxy-4-methylcoumarandione-2,3, m.p. 165° (29).]

*Behavior of  $\bar{C}$  with organic acids or their derivatives.* [ $\bar{C}$  with silver oxalate in dry ether does *not* yield the unknown oxalic anhydride but instead immediately evolves CO + CO<sub>2</sub> until all the salt has disappeared (1).]

[ $\bar{C}$  with organic acids, their salts, or their anhydrides, gives the corresp. acid chlorides in good yield (19); furthermore under appropriate conditions  $\bar{C}$  with aromatic acids gives good yields (50) of the corresp. arom. anhydrides; for numerous examples see indic. refs.]

*Behavior of  $\bar{C}$  with amines or their derivatives.*  $\bar{C}$  with primary or secondary amines (2 moles) reacts normally as a bifunctional acid chloride yielding corresp. *N*-substituted oxamides (see also below under ①'s).

[Note, however, that with amine salts reaction takes a different course. — E.g.,  $\bar{C}$  with aniline hydrochloride at 15° evolves HCl and gives (100% yield (62)) oxanilyl chloride, C<sub>6</sub>H<sub>5</sub>.NH.CO.CO.Cl [Beil. XII-283, XII<sub>1</sub>-(206)], pr. from pet. ether, m.p. 82.5°;  $\bar{C}$  with  $\alpha$ -naphthylamine.HCl in chlorobenzene at 15° similarly yields (12) *N*-( $\alpha$ -naphthyl)oxamidyl chloride, C<sub>10</sub>H<sub>7</sub>.NH.CO.CO.Cl, m.p. 86° (62);  $\bar{C}$  with  $\beta$ -naphthylamine HCl similarly yields (62) *N*-( $\beta$ -naphthyl)oxamidyl chloride, ndls. from C<sub>6</sub>H<sub>6</sub>, m.p. 114–115° dec. (62). — Note that these prods. with condensing agents such as  $AlCl_3$ .FeCl<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> ring-close with loss of HCl to yield homologs of isatin: e.g., *N*-( $\alpha$ -naphthyl)oxamidyl chloride +  $AlCl_3$  at 80–85° for 8 hrs. gives (63) 6,7-benzoisatin [Beil. XXI-524, XXI<sub>1</sub>-(414)] ("1,2-naphthisatin"), red ndls., m.p. 255°; *N*-( $\beta$ -naphthyl)oxamidyl chloride with  $AlCl_3$  in

nitrobenzene at 80° gives (75-80% yield (63)) 4,5-benzoisatin ("2,1-naphthisatin") [Beil. XXI-525, XXI-(415)], m.p. 252-253°.]

[Note, furthermore, that the above general synthesis of isatin homologs can be carried out starting with *N*-acylated arom. amines: e.g.,  $\bar{C}$  with Na salt of *N*-(*p*-toluenesulfonyl)-*p*-toluidide in  $CS_2$  splits out NaCl giving (64) *N*-(*p*-toluenesulfonyl)-*N*-(*p*-tolyl)oxamidyl chloride, cryst. from  $C_6H_6$ , m.p. 91-93° (64); this prod. on bfg. with  $AlCl_3$  loses HCl and ring-closes to *N*-(*p*-toluenesulfonyl)-5-methylisatin, cryst. from AcOH or  $C_6H_6$ , m.p. 202-205°, hydrolysis of which by stdg. 1 day with conc  $H_2SO_4$  yields (64) 5-methylisatin [Beil. XXI-509, XXI-(401)], red ndls. from aq. or alc., m.p. 187°.]

[For analogous reactn. of  $\bar{C}$  with secondary arom. amines and ring closure to *N*-substituted isatins see (65).]

[ $\bar{C}$  with *N,N*-dimethylaniline gives various prods. according to conditions:  $\bar{C}$  (1 mole) with dimethylaniline (2 moles) in dry ether in cold gives (100% yield (66)) (*p*-dimethylaminobenzoyl)formyl chloride,  $(CH_3)_2N.C_6H_4.CO.Cl$ , stable only in soln. and on treatment with aq. giving (80% yield (66)) (*p*-dimethylaminobenzoyl)formic acid, golden-yel. lfts. from AcOH or MeOH, m.p. 186-187° dec.,  $\bar{C}$  (1 mole) with dimethylaniline (4 moles) in  $C_6H_6$ , stood 15 hrs. in cold, then heated gives tetramethyldiaminobenzil + the carbinol base of "Crystal Violet" (for many further details see (66)); for use of  $\bar{C}$  in prepn. of "Crystal Violet" see (67).]

[ $\bar{C}$  with *o*-aminothiophenol (80) or with its Zn salt (68) at 60-80° until reactn. begins, then htd. at 100° for 1 hr., gives (60% yield (68)) bis-2,2'-benzothiazolyl [Beil. XXVII-744, XXVII-(626)], m.p. 300.5° u.c. (68), 304° (80); similarly  $\bar{C}$  with Zn salt of *o*-aminoselenophenol gives (69) bis-2,2'-benzoselenazolyl, m.p. 314° u.c. (69).]

*Behavior of  $\bar{C}$  with certain amides.* [ $\bar{C}$  with urea directly or in ether gives (8) (21) parabanic acid (*N,N'*-oxalylurea) [Beil. XXIV-449, XXIV-(401)], cryst. from alc., m.p. 244°, accompanied by more or less oxaldureide, insol, m.p. 270-275° dec. (8). —  $\bar{C}$  with *N,N'*-dimethylurea gives (70% yield (8)) *N,N'*-dimethylparabanic acid [Beil. XXIV-453, XXIV-(404)], m.p. 154° (8). —  $\bar{C}$  with *N*-phenylurea in ether refluxed 3 hrs. gives (88% yield (8)) *N*-phenylparabanic acid [Beil. XXIV-454, XXIV-(405)], lfts. from alc., m.p. 213-214° cor., after sintering at 208° (8). —  $\bar{C}$  with *N,N'*-diphenylurea in ether gives (100% yield (8)) *N,N'*-diphenylparabanic acid [Beil. XXIV-455, XXIV-(405)], ndls. from alc., m.p. 202° cor., after prelim. sintering (8).]

[For examples of condensation of  $\bar{C}$  with various other amides see (21) (70) (71) (73); with various amino acids see (72).]

*Behavior of  $\bar{C}$  with carbonyl compounds.* [ $\bar{C}$  with ketones often acts like  $PCl_5$  by replacing the oxygen with 2 chlorine atoms with evolution of CO +  $CO_2$  for many specific examples see (74); also note that  $\bar{C}$  with vanthone (1:7275) gives (75) (76) xanthone dichloride;  $\bar{C}$  with *N*-methyl- or *N*-phenylacridone gives (77) dichlorides.]

*Behavior of  $\bar{C}$  with organometallic compounds.* [ $\bar{C}$  with nickel carbonyl reacts according to equation  $Ni(CO)_4 + (COCl)_2 \rightarrow NiCl_2 + 6CO$  (13) —  $\bar{C}$  with  $Et_2Cd$  (from  $C_2H_5MgBr + CdCl_2$ ) gives (27% yield (77)) 3-ethylhexanol-3-one-4 (diethyl-propionyl-carbinol) [Beil. I-841, I-(881)], b.p. 178-179° (78). — For interference of  $\bar{C}$  with the Michler's ketone test for  $RMgX$  cpds. see (79).]

- ① Oxalyl (di)chloride/1,4-dioxane mol. cpd.: ndls. or pr. from pet. ether, m.p. 67-68° (81). [From  $\bar{C}$  with 5 wt. pts. dioxane-1,4 (1:6400) in 25 vols. pet. ether at -5° in stream of dry air or  $N_2$ ; the 1:1 mol. cpd. ppts. in 71-78% yield (81). — Note that this prod. may with aniline be converted to oxanilide (see below) or may be dislvd. in excess stand. alk. and titrated back with stand. acid; furthermore, on stdg. in moist air, it is quant. converted to oxalic acid dihydrate (1:0445). — Note also that

under same conditions no ppt. results with acetyl chloride (3:7065), benzoyl chloride (3:6240), malonyl (di)chloride (3:9030), succinyl (di)chloride (3:6200), fumaryl (di)chloride (3:5875), *sym.*-phthaloyl (di)chloride (3:6900), *unsym.*-phthaloyl (di)chloride (3:2395) or terephthaloyl (di)chloride (3:2205) (81).]

① Oxanilide (oxalic acid dianilide): pl. from  $C_6H_6$  or nitrobenzene m.p.  $251^\circ$  (21)  $252-253^\circ$  (71). [From  $\bar{C}$  + aniline in cold ether or from  $\bar{C}$  + aniline hydrochloride in boilg.  $C_6H_6$  (21); note that by virtue of the relative insolubility of oxanilide and its easy quantitative formn. it is often employed as means for quant. detn. of  $\bar{C}$  cf. (1). — Note also that the half reactn. prod. oxanilyl chloride m.p.  $82.5^\circ$  has been mentioned above in main text.]

— Oxal-bis-(*p*-toluidide): m.p.  $268^\circ$  (cf. 1:0445).

— Oxal-bis-( $\alpha$ -naphthalide): m.p.  $234^\circ$ .

— Oxal-bis-( $\beta$ -naphthalide): m.p.  $275^\circ$ .

② Oxal-bis-(phenylhydrazide): cryst. from alc. or AcOH m.p.  $278^\circ$  (82). [From  $\bar{C}$  (1 mole) in  $C_6H_6$  with phenylhydrazine (4 moles) in dry ether (82).]

— Oxal-bis-(*p*-nitrophenylhydrazide): unreported.

— Oxal-bis-(2,4-dinitrophenylhydrazide): yel. cryst. from alc. m.p.  $202^\circ$  after darkening at about  $270^\circ$ . [Prepd. indirectly.]

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3:5075 METHYL CHLOROFORMATE  $\text{Cl.COOCH}_3$   $\text{C}_2\text{H}_3\text{O}_2\text{Cl}$  Beil. III - 9  
 ("Methyl chlorocarbonate") III<sub>1</sub>-(5)  
 III<sub>2</sub>-(9)

B.P. 72-73° at 767 mm. {1}	$D_4^{20} = 1.2231$ {1}	$n_D^{20} = 1.38675$ {1}
71.4-72.4° {2}		
71.2-71.5° at 733 mm. {3}	$D_4^{16.5} = 1.2240$ {6}	
71.4° cor. {4}		
71.0-71.5° at 760 mm. {7}		
71-71.5° {20}		
69° at 720 mm. {5}		

[See also ethyl chlorocarbonate (3:7295).]

$\tilde{\text{C}}$  is colorless liquid with penetrating odor and strong lachrymatory properties.

[For prepn. of  $\tilde{\text{C}}$  from carbonyl chloride (phosgene) (3:5000) with MeOH see {8} {9} {7} {4} {10} {20} {21}; from methyl formate (1:1000) with  $\text{Cl}_2$  see {11} {12} (chloromethyl chloroformate (3:5275) is also formed); from pentachloroethyl chloroformate [Beil. III-13, III<sub>1</sub>-(6)] {13} or from bis-(trichloromethyl) oxalate [Beil. III-17] {14} or from methyl trichloromethyl carbonate [Beil. III-17 III<sub>1</sub>-(8) III<sub>2</sub>-(15)] {15} with MeOH see indic. refs.]

Pyrolysis of  $\tilde{\text{C}}$ . Unlike the case of ethyl chloroformate (3:7295) the pyrolysis of  $\tilde{\text{C}}$  appears to have been little studied: in quinoline the decomposition temp. is given {16} {17} as 36°; presumably the decomposition yields MeCl (3:7005) +  $\text{CO}_2$ .

Reactions of the  $-\text{COOMe}$  group of  $\tilde{\text{C}}$ .  $\tilde{\text{C}}$  is not readily decomposed by cold aq. {4} {11} {18} and can even be washed to remove alc.;  $\tilde{\text{C}}$  on boilg. with aq. or dil. acid or dil. alk., however, is readily hydrolyzed yielding MeOH (1:6120) +  $\text{CO}_2$  + HCl.

[ $\tilde{\text{C}}$  with  $\text{Cl}_2$  under various conditions {19} {20} {21} {22} {23} yields successively chloromethyl chloroformate (3:5275) dichloromethyl chloroformate (3:5315) and ultimately trichloromethyl chloroformate ("diphosgene") (3:5515).]

[ $\tilde{\text{C}}$  (10% excess) with  $\text{MeHSO}_4$  at 100° under reflux for 6-8 hrs. gives (100% yield {24})

3:5085 1,1,1-TRICHLOROETHANE  $\text{CH}_3\text{CCl}_3$   $\text{C}_2\text{H}_3\text{Cl}_3$   
(Methylchloroform)

Beil. I - 85

I<sub>1</sub>—I<sub>2</sub>-(55)

B.P.

F.P.

74.5°	at 767 mm. (1)	−30.4° (4)	$D_4^{20} = 1.3492$	$n_D^{20} = 1.43838$ (4)
74.9°	at 768.3 mm. (2)	−32.2° (8)		1.4384 (1)
74.1°	at 760 mm. (3)	−32.7° (9)		1.4379 (9)
74°	(9)	−32.96° (21)		
73.9° cor.	at 760 mm. (4)			
73.86–73.94° cor.	(5)			
73.8°	(6)			
74.1–74.5°	at 747.5 mm. (7)			

Liquid. — [For f.p./compn. data on mixts. of  $\bar{\text{C}}$  with 2,2-dichloropropane (3:7140) or with pentachloroethane (3:5880) see (8); for extensive study of vap. press., heat capacity, and other thermodynamic props. see (21); for soly. of aq. in  $\bar{\text{C}}$  see (22).] [For use of  $\bar{\text{C}}$  as dry cleaning fluid see (10); for use of  $\bar{\text{C}}$  in dewaxing of oils see (11).] [For detn. of  $\bar{\text{C}}$  in air by thermal decompn. method see (23).]

[For prepn. of  $\bar{\text{C}}$  from 1,1-dichloroethane (ethylidene dichloride) (3:5035) by actn. of  $\text{Cl}_2$  see (12) (13) (7); for manufacture of  $\bar{\text{C}}$  from 1,1-dichloroethylene (vinylidene dichloride) (3:5005) by cat. addn. of  $\text{HCl}$  see (14) (15).]

$\bar{\text{C}}$  with  $\text{Ca}(\text{OH})_2$  at ord. temp. loses  $\text{HCl}$  yielding (16) 1,1-dichloroethylene (3:5005).

$\bar{\text{C}}$  with aq. under specified conditions and catalyst hydrolyzes to yield (17) (18)  $\text{AcOH}$ ,  $\text{AcCl}$ , or  $\text{Ac}_2\text{O}$ .

[For study of actn. of fluorine on  $\bar{\text{C}}$  see (19).]

$\bar{\text{C}}$  with phenol + aq.  $\text{NaOH}$  gives (20) small yield of a mixt. of *o*-hydroxyacetophenone (1:1745) and *p*-hydroxyacetophenone (1:1527). [For impt. clarification of previous misapprehension of this reactn. see (20).]

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(20) *Conn. J. Am. Chem. Soc.* 57, 579, 580 (1935).

(22) Staverman, *Rec*  
(23) Smyth, *Ind. Eng.*

3:5166 CARBON TETRACHLORIDE  
(Tetrachloromethane) $\text{CCl}_4$ 

Beil. I - 64

 $I_1$ -(12) $I_2$ -(22)

B.P.			F.P.		
77.4°	at	774 mm. (1)	-22° (28) (51)	$D_4^{20} = 1.57486$ (7)	
77.2°	at	766 mm. (2)	-22.3° (52)	$n_D^{25.2} = 1.45767$ (65)	
76.6°	at	760 mm. (3)	-22.5° (17)	1.45707 (65)	
		(20)	(29)	$D_4^{25} = 1.5850$ (54)	
76.87°	at	749 mm. (4)	-22.6° (30)	1.58472 (55)	
76.83°	at	760 mm. (83)	(83)	1.58469 (22)	
76.8°		(5) (87)	-22.7° (31)	1.58447 (5)	
76.75°	at	760 mm. (6)	-22.81° (15)	1.58445 (13)	
		(7) (19)	-22.83° (32)	1.58443 (7)	
76.74°	at	760 mm. (8)	-22.86° (33)	1.58434 (56)	
		(9)	(34)	1.58426 (57)	
76.71°	at	760 mm. (10)	-22.87° (35)	1.58414 (58)	
76.70-76.74°	at	760 mm. (11)	(36)	1.5835 (23) (59) (166)	
76.7° u.c.	at	754 mm. (12)	-22.89° (37)	$n_D^{25} = 1.45936$ (21)	
76.69°	at	760 mm. (55)	-22.6° (38)	1.45759 (13)	
76.886°	at	760 mm. (13)	(39) (53)	1.4574 (66)	
76.685°	at	760 mm. (14)	-22.95° (7)	1.45732 (67)	
76.66°	at	760 mm. (15)	(40) (41) (42)	1.45724 (166)	
76.6°	at	760 mm. (48)	-22.968° (87)	1.4546 (68)	
76.58-76.66°	at	761 mm. (16)	-23.6 (43) (44)	$n_D^{23.8} = 1.45786$ (69)	
76.52°	at	760 mm. (49)	(45) (153)	$D_4^{20} = 1.59472$ (60)	
76.5°	at	759 mm. (17)	-23.4° (46)	1.5944 (11)	
76.5° (18)	at	760 mm. (19)	-23.5° (47)	1.5942 (61)	
76.45-76.56°	at	760 mm. (21)		1.59467 (7)	
76.4°		(50) (73)	See also Notes	1.5940 (61)	
76.22-76.38°	at	741 mm. (22)	4, 5, and 6.	(62) (63)	
76.2°	at	745 mm. (56)		1.5924 (64)	
76.1°	at	743 mm. (23)		1.46023 (50)	
76°	at	733 mm. (24)		$n_D^{20} = 1.4630$ (70)	
75.55°	at	760 mm. (19)		1.461 (15)	
75.4°	at	760 mm. (25)		1.46048 (11)	
		(19)		1.46044 (13)	
75.3-75.4°	at	729 mm. (56)		1.46041 (10)	
75.2°	at	751.4 mm. (26)		1.46040 (55)	
74.95°	at	720 mm. (10)		1.46026 (165)	
74.4-74.5°	at	709 mm. (30)		1.46023 (27)	
73.50°	at	687 mm. (27)		$D_4^{15} = 1.60370$ (7)	
72.0°	at	643.2 mm. (2)		1.6011 (23)	
71.0°	at	663 mm. (23)		See also Note 7.	
65.0°	at	659 mm. (23)		$n_D^{19.68} = 1.46694$ (10)	
62.0°	at	506 mm. (23)			
60.0°	at	416 mm. (2)		$n_D^{16.80} = 1.46266$ (10)	
58.5°	at	443 mm. (23)			
59.5°	at	398.86 mm. (2)		$n_D^{15} = 1.46325$ (163)	
54.8°	at	386 mm. (23)		1.46305 (7)	
50.0°	at	328 mm. (23)		1.4629	

## B.P. (Cont.)

46.3°	at 282 mm. (23)	$n_D^{12.3} = 1.4056$ (71)
42.0°	at 236 mm. (23)	
36.0°	at 170.95 mm. (2)	$n_D^{12} = 1.4674$ (71)
31.0°	at 140 mm. (23)	
25.0°	at 110 mm. (23)	$n_D^{11.19} = 1.40589$ (10)
		$n_D^{10.5} = 1.4601$ (10)

See also Notes 1, 2, and 3.

Note 1. For studies of vap. press. of  $\bar{C}$  over range  $-20^\circ$  to  $+283^\circ$  (72) and range  $+10.2$  to  $70.4^\circ$  (73) see indic. refs.

Note 2. For studies of effect on b.p., vap. press., vapor density of very intensive drying see (74) (75) (70) (77) (70) (80).

Note 3. For study of detn. of b.p. range of  $\bar{C}$  as method of estimation of impurities see (81).

Note 4. For studies on effect of prior history of sample on detn. of f.p. of  $\bar{C}$  see (32) (52) (51).

Note 5. For studies of influence of high press. of f.p. see (41) (83).

Note 6. Solid  $\bar{C}$  has a transition point variously determined as follows:  $-47^\circ$  (85) cf. (17),  $-47.55^\circ$  (33),  $-47.03^\circ$  (15),  $-47.00^\circ$  (32) (36),  $-47.84^\circ$  (30),  $-48.1^\circ$  (47),  $-48.5^\circ$  (80),  $-48.54^\circ$  (87).

Note 7. For studies of density of  $\bar{C}$  over ranges  $-180^\circ$  to  $-80^\circ$  (88),  $0^\circ$  to  $283^\circ$  (crit. temp.) (72), and  $-18^\circ$  to  $+60^\circ$  (80) see indic. refs.

[See also methylene (di)chloride (3:5020) and chloroform (3:5050).]

MISCELLANEOUS PHYSICAL PROPERTIES OF  $\bar{C}$ 

## VARIOUS SOLUBILITY RELATIONS

With water.  $\bar{C}$  is only very slightly sol. aq. and is eas. volatile with steam; e.g., 100 g. aq. at  $0^\circ$  dis. 0.007 g.  $\bar{C}$  (91), at  $10^\circ$  0.083 g. (91), at  $15^\circ$  0.081 g. (8), at  $20^\circ$  0.090 g. (91), at  $30^\circ$  0.077 g. (8), 0.085 g. (91); for study of salting-out effect of KCl or  $MgSO_4$  see (92). — For studies of soly. of aq. in  $\bar{C}$  at  $0^\circ$  (93),  $10^\circ$  (94),  $20^\circ$  (94),  $25^\circ$  (93), and  $30^\circ$  (93) (94) see indic. refs.; for study of reciprocal soly. of  $\bar{C}$  + aq. see (95).

With various inorganic compounds. (For data on soly. in  $\bar{C}$  of  $H_2$  (96),  $O_2$  (97) (94),  $O_3$  (99) (100), air (96),  $N_2$  (at high pressure) (101), NO (107),  $NO_2$  (102),  $N_2O$  (96),  $NH_3$  (103),  $H_2S$  (103),  $SO_2$  (90) (110),  $HI$  (103) (104) (105) (100),  $HBr$  (100),  $Cl_2$  (108) (109) (110), or  $CO_2$  (111) (112) see indic. refs. — For data on soly. of  $I_2$  in  $\bar{C}$  see (113) (121) (122) (123) (124) (125); for study of nature of  $I_2$  solns. in  $\bar{C}$  see (114); for soly. of  $I_2$  in  $CCl_4$  vapor see (115). — For data on soly. of sulfur in  $\bar{C}$  see (128) (129) (130). — For data on soly. of  $AlCl_3$  in  $\bar{C}$  see (135).]

With various organic compounds. (For data on soly. in  $\bar{C}$  of ethane (110), ethylene (110) under high press. (101), acetylene (110), dimethyl ether (117),  $CH_2Cl$  (117) (118),  $COCl_2$  (110) (120) see indic. refs.)

BINARY SYSTEMS CONTAINING  $\bar{C}$ 

(See also azeotropes containing  $\bar{C}$ )

$\bar{C}$  with various inorganic compounds.  $\bar{C} + Cl_2$ : for f.p./compn. data and diag. (note that 5 different cpds. are formed) see (29) cf. (17) (126). —  $\bar{C} + Br_2$ : for f.p./compn. data and diag. (eutectic has f.p. about  $-47.0^\circ$  and conts. about 82.7 mole %  $\bar{C}$  (38)) see (38) cf. (125). —  $\bar{C} + I_2$ : see above under soly. of  $I_2$  in  $\bar{C}$ . —  $\bar{C} + I-Cl$ : for f.p./compn. data and

diag. (series of solid solns.) see (31) cf. (127). —  $\bar{C}$  +  $SO_2$ : for f.p./compn. data and diag see (131) —  $\bar{C}$  +  $H_2S$ : for f.p./compn. diag see (132). —  $\bar{C}$  +  $N_2O_4$ : for f.p./compn. data and diag. see (133) —  $\bar{C}$  +  $PCl_5$ : for formn. of compd.  $2PCl_5 \cdot CCl_4$  see (134). —  $\bar{C}$  +  $PBr_5$ : for formn. of 2 cpds see (134). —  $\bar{C}$  +  $TiCl_4$ : for f.p./compn. data and diag see (53); for b.p. and liq. vapor compn see (48)

$\bar{C}$  with org. cpds. of Order 1.  $\bar{C}$  + *n*-heptane (1:8575): for study of ht. of mixing see (136); for  $n_D^{20}$ /compn. sec (165) —  $\bar{C}$  +  $C_6H_6$  (1:7400): for f.p./compn. data and diag see (137) (138) (90), for data on  $D_4^{20}$  (12),  $D_4^{23}$  (12),  $D_4^{25}$  (12),  $D_4^{25}$  (57) (140) (166), and  $D_{30}^{20}$  (141) versus compn. sec indie refs., for  $n_D^{14.5}$  (142),  $n_D^{20}$  (10), or  $n_D^{25}$  (65) (68) (166) versus compn. sec indie refs.; for refractive indices at various wave lengths see (67); for data on b.p. at 720 mm (10), vap. press. (2) (58) (10) (65) (143) (163), heat of mixing (141) (144), liq.-vapor equil (145), or study of distn. through packed column (139) see indie refs. —  $\bar{C}$  + toluene (1:7403): for data on vap. press. (4) (143),  $D_4^{20}$  (12) cf. (4),  $D_4^{25}$  (166),  $n_D^{15}$  (146), and  $n_D^{25}$  (4) (166) see indie refs. —  $\bar{C}$  + cyclohexane (1:8405): for f.p./compn. data (147),  $D_4^{20}$  (62),  $D_4^{25}$  (140) (58),  $n_D^{25}$  (140) see indie refs.

$\bar{C}$  +  $MeOH$  (1:6120): for  $D_4^{25}$  and  $n_D^{25}$ /compn. sec (151). —  $\bar{C}$  +  $EtOH$  (1:6130): for vap. press. data/compn. sec (148) (149); for  $D_4^{25}$  (59) (166) and  $n_D^{15}$  (167) or  $n_D^{25}$  (166) see indie refs. —  $\bar{C}$  + *n*- $PrOH$  (1:6150): for  $n_D^{25}$ /compn. sec (66) —  $\bar{C}$  + *n*- $BuOH$  (1:6180): for  $n_D^{20}$ /compn. sec (185) —  $\bar{C}$  + *isoAmOH* (1:6200): for  $D_4^{25}$  and  $n_D^{25}$  versus compn. sec (166) —  $\bar{C}$  + cyclohexanol (1:6415): for f.p./compn. data see (150)

$\bar{C}$  + diethyl ether (1:6110): for data on f.p./compn. (152),  $D_4^{20}$  (62),  $D_4^{25}$  (166), and  $n_D^{25}$  (166) see indie refs. —  $\bar{C}$  + diisopropyl ether (1:6125): for  $D_4^{20}$ /compn. sec (62). —  $\bar{C}$  + diazane-1,4 (1:6400): for  $D_4^{20}$ /compn. sec (62). —  $\bar{C}$  + anisole (1:7445): for f.p./compn. data and diag. sec (153) —  $\bar{C}$  + diphenyl ether (1:7125): for f.p./compn. data and diag. sec (153)

$\bar{C}$  + acetone (1:5400): for f.p./compn. data and diag. sec (90) (147); for  $D_4^{20}$  (62),  $D_4^{25}$  (59), and  $n_D^{15}$  (166) versus compn. sec indie refs.

$\bar{C}$  +  $MeOAc$  (1:3005): for  $D_4^{25}$  and  $n_D^{25}$  versus compn. sec (166) —  $\bar{C}$  +  $EtOAc$  (1:3015): for f.p./compn. data and diag. sec (152); for data on vap. press. (65) (192),  $D_4^{25}$  (166),  $n_D^{20}$  (27),  $n_D^{25}$  (166) cf. (65) versus compn. sec indie refs. —  $\bar{C}$  +  $EtOBz$  (1:3721): for  $D_4^{20}$  compn. sec (61) —  $\bar{C}$  + diethyl carbonate (1:3150): for  $D_4^{25}$ /compn. sec (5).

$\bar{C}$  with org. cpds. of Order 2.  $\bar{C}$  + nitrobenzene: for f.p./compn. data and diag. (eutectic, f.p.  $-34.5^\circ$ , conts. 81.5 wt. %  $\bar{C}$  (44)) see (41) cf. (138); for  $D_4^{20}$ ,  $D_4^{25}$ , and  $n_D^{20}$  versus compn. sec (154) —  $\bar{C}$  + aniline: for f.p./compn. data (147) and  $D_4^{25}$ /compn. (155) see indie refs. —  $\bar{C}$  + quinoline: for  $D_4^{20}$ /compn. sec (62)

$\bar{C}$  with org. cpds. of Order 3.  $\bar{C}$  +  $CH_2Cl_2$  (3:5020): for data on b.p.,  $D_4^{20}$ , and liq.-vapor equilibria see (156) —  $\bar{C}$  +  $CHCl_3$  (3:5030): for f.p./compn. data and diag. (eutectic, f.p.  $-81.1^\circ$ , conts. 49.4 wt. %  $\bar{C}$  (16)) (38) (147) (157) cf. (125) see indie refs.; for  $D_4^{20}$ /compn. sec (156) (158) cf. (12); for  $n_D^{25}$  compn. sec (166); for b.p. and liq.-vapor equil. see (156). —  $\bar{C}$  + 1,1-dichloroethane (3:5035): for b.p.,  $D_4^{20}$ , and liq.-vapor equil. see (156). —  $\bar{C}$  + 1,2-dichloroethane (3:5130): for data on b.p. (49) (159), liq.-vapor equil. (49) (159) (160),  $D_4^{20}$ /compn. (49) see indie refs. —  $\bar{C}$  + pentachloroethane (3:5880): for f.p./compn. data and diag. sec (157) —  $\bar{C}$  + 1,1,2,2-tetrachloroethylene (3:5160): for f.p./compn. data (15), vap. press. (3) and liq.-vapor equil. (3) see indie refs. —  $\bar{C}$  + 2,2-dichloropropane (3:7140): for f.p./compn. data sec (45). —  $\bar{C}$  + *tert*-butyl chloride (3:7045): for f.p./compn. data and diag. (complete series of solid solns.) see (47) (161) —  $\bar{C}$  + chlorobenzene (3:7903): for  $D_4^{20}$ /compn. sec (61)

$\bar{C}$  with org. cpds. of higher orders.  $\bar{C}$  +  $CBBr_3$ : for extensive study of this system see (162); for  $D_4^{25}$ /compn. sec (54). —  $\bar{C}$  +  $C_2H_5Br$ : for  $D_4^{20}$ /compn. sec (158) —  $\bar{C}$  + 1,2-dibromoothane: for f.p./compn. data and diag. sec (138).



$\bar{C}$  +  $CHI_3$ : for f.p./compn. data see {45}. —  $\bar{C}$  +  $Etl$ : for vap. press., liq.-vapor equil., and  $n_D^{25.2}$  see {65}.

$\bar{C}$  +  $CS_2$ : for f.p./compn. data {147}, study of distn. {164} {168},  $D_{20}^{20}$ /compn. {164},  $D_{25}^{25}$ /compn. {12}, and  $n_D^{15}$ /compn. {168} see indic. refs.

### TERNARY SYSTEMS CONTAINING $\bar{C}$

(See also azeotropes containing  $\bar{C}$ )

$\bar{C}$  +  $MeOH$  (1:6120) +  $aq.$ : for studies of phase relations {169} cf. {170} and colloidal character {171} see indic. refs. —  $\bar{C}$  +  $EtOH$  (1:6130) +  $aq.$ : for data on soly. relations incl. density and refractive indices see {173} cf. {170}. —  $\bar{C}$  +  $EtOH$  (1:6130) +  $C_6H_6$  (1:7400): for data on vap. press see {148} —  $\bar{C}$  +  $EtOH$  (1:6130) + *glycerol* (1:6540): for study of soly. relations see {172}. —  $\bar{C}$  +  $n-PrOH$  (1:6150) +  $aq.$ : for data and diag. of soly. relations at 20°, and  $n_D^{25}$ /compn., see {66} cf. {170}. —  $\bar{C}$  +  $AcOH$  (1:1010) +  $C_6H_6$  (1:7400): for data on density and  $n_D^{25}$  see {68}; for vap. press. data see {2}. —  $\bar{C}$  + *toluene* (1:7405) + *1,2-dibromoethane*: for extensive study see {4} {174}. —  $\bar{C}$  +  $CH_2Cl_2$  (3:5020) +  $CHCl_3$  (3:5050): for f.p./compn. data (ternary eutectic, f.p. -111.4°, conts. 13 wt. %  $\bar{C}$  + 60 wt. %  $CH_2Cl_2$  + 27 wt. %  $CHCl_3$ ) see {46}.

### BINARY AZEOTROPES CONTAINING $\bar{C}$

$\bar{C}$  +  $MeOH$  (1:6120):  $\bar{C}$  forms with  $MeOH$  a const.-boilg. mixt., b.p. 55.70° at 760 mm., contg. 79.44 wt. % = 44.5 mole %  $\bar{C}$  {175}, b.p. 54.4° at 734 mm., contg. 77 wt. %  $\bar{C}$  {176}, b.p. 54.2° at 718 mm., contg. 79 wt. %  $\bar{C}$  {176}; cf. also {177} {178}. —  $\bar{C}$  +  $EtOH$  (1:6130):  $\bar{C}$  forms with  $EtOH$  a const.-boilg. mixt., b.p. 64.05° {175}, 65.08° {179} at 760 mm., contg. 84.15 wt. % = 61.3 mole % {175}  $\bar{C}$ ; cf. also {180} {181}; for effect of press. on this azeotrope see {182}. —  $\bar{C}$  +  $n-PrOH$  (1:6150):  $\bar{C}$  forms with  $n-PrOH$  a const.-boilg. mixt., b.p. 72.8° {175}, 73.1° {179} at 760 mm., contg. 83.5 wt. % = 75 mole % {175}  $\bar{C}$ ; cf. also {183}. —  $\bar{C}$  + *iso* $PrOH$  (1:6135):  $\bar{C}$  forms with *isopropyl alc.* a const.-boilg. mixt., b.p. 67.5° {175}, 68.95° {184}, contg. about 82 wt. % {175} {184} = 64 mole %  $\bar{C}$ ; cf. also {183}. —  $\bar{C}$  + *n-BuOH* (1:6180):  $\bar{C}$  forms with *n-butyl alc.* a const.-boilg. mixt., b.p. 76.55° at 760 mm., contg. 97.5 wt. %  $\bar{C}$  {179}. —  $\bar{C}$  + *iso* $BuOH$  (1:6165):  $\bar{C}$  forms with *isobutyl alc.* a const.-boilg. mixt., b.p. 75.8° at 760 mm., contg. 94.5 wt. % = 89 mole %  $\bar{C}$  {175} cf. {183} {186}. —  $\bar{C}$  + *ter-BuOH* (1:6140):  $\bar{C}$  forms with *ter-butyl alc.* a const.-boilg. mixt., b.p. 69.5° {175}, 70.5° {185} at 760 mm., contg. 83 wt. % {175}, 76 wt. % {185}  $\bar{C}$ . —  $\bar{C}$  + *ter-AmOH* (1:6160):  $\bar{C}$  forms with *dimethyl-ethyl-carbinol* a const.-boilg. mixt., b.p. about 76° at 760 mm., contg. about 95 wt. %  $\bar{C}$  {185}. —  $\bar{C}$  + *allyl alc.* (1:6145):  $\bar{C}$  forms with *allyl alc.* a const.-boilg. mixt., b.p. 72.5°, contg. 79.5 mole %  $\bar{C}$  {187}.

$\bar{C}$  + *acetone* (1:5400):  $\bar{C}$  forms with *acetone* a const.-boilg. mixt., b.p. 55.9° at 763 mm. {188}, about 56° at 760 mm. {185}, contg. about 11.5 wt. % {185}  $\bar{C}$ . —  $\bar{C}$  + *methyl ethyl ketone* (1:5405):  $\bar{C}$  with *methyl ethyl ketone* forms a const.-boilg. mixt., b.p. 73.8° at 760 mm., contg. 71 wt. % = 53.4 mole % {175}  $\bar{C}$ .

$\bar{C}$  +  $AcOH$  (1:1010):  $\bar{C}$  forms with  $AcOH$  a const.-boilg. mixt., b.p. about 77° at 760 mm., contg. about 97 wt. %  $\bar{C}$  {189}.

$\bar{C}$  +  $EtOAc$  (1:3015):  $\bar{C}$  forms with *ethyl acetate* a const.-boilg. mixt., b.p. 74.75° at 760 mm. {175} {190}, contg. 57 wt. %  $\bar{C}$  {190}; b.p. 76.15° at 789.2 mm. contg. 55.6 mole %  $\bar{C}$  {191}; b.p. 71.56° at 685.0 mm. contg. 58.2 mole %  $\bar{C}$  {27}; b.p. 66.72° at 583.7 mm. contg. 60.75 mole %  $\bar{C}$  {191}; b.p. 61.32° at 484.5 mm. contg. 63.75 mole %  $\bar{C}$  {191}; b.p. 55.22° at 385.2 mm. contg. 67.75 mole %  $\bar{C}$  {191}; b.p. 47.36° at 285.7 mm. contg. 72.6 mole %  $\bar{C}$  {191}: for study of thermodynamics of system see {193}. —  $\bar{C}$  + *methyl propionate* (1:3020):  $\bar{C}$  forms with *methyl propionate* a const.-boilg. mixt., b.p. 75.5° at 760 mm.,

contg. 60 wt. % = 46 mole % (175); b.p.  $76^\circ$  at 760 mm. contg. about 75 wt. % (194)  $\bar{C}$ . —  $\bar{C}$  + *n*-Pr formate (1:2030):  $\bar{C}$  forms with *n*-propyl formate a const.-boilg. mixt., b.p.  $74.6^\circ$  at 760 mm., contg. about 69 wt. %  $\bar{C}$  (184).

$\bar{C}$  + nitromethane:  $\bar{C}$  forms with nitromethane a const.-boilg. mixt., b.p.  $71.3^\circ$  at 760 mm., contg. about 83 wt. %  $\bar{C}$  (184). —  $\bar{C}$  + 1,2-dichloroethane (3:5130):  $\bar{C}$  forms with ethylene dichloride a const.-boilg. mixt., b.p.  $75.30^\circ$  at 760 mm., contg. about 70 mole %  $\bar{C}$  (49) cf. (159); b.p. about  $76^\circ$  at 760 mm. contg. 79 wt. %  $\bar{C}$  (185).

### TERNARY AZEOTROPES CONTAINING $\bar{C}$

$\bar{C}$  + EtOH (1:6130) + aq: this system forms a ternary two-phase const.-boilg. mixt., b.p.  $61.8^\circ$  at 760 mm. (181) (175), contg. 86.3 wt. % = 57.6 mole %  $\bar{C}$  + 10.3 wt. % = 23.0 mole % EtOH + 3.4 wt. % = 19.4 mole % aq; for use of this azeotrope in detn. of water content of wood see (195). —  $\bar{C}$  + *n*-PrOH (1:6150) + aq: this system forms a ternary two-phase const.-boilg. mixt., b.p.  $54.4^\circ$  at 760 mm., contg. 54.4 mole %  $\bar{C}$  + 18.0 mole % *n*-propyl alc. + 27.6 mole % aq. (175). —  $\bar{C}$  + allyl alc. (1:6145) + aq: this system forms a const.-boilg. mixt., b.p.  $65.4^\circ$  at 760 mm., contg. 90.43 wt. % = 64.5 mole %  $\bar{C}$  + 5.44 wt. % = 10.4 mole % allyl alc. + 4.13 wt. % = 25.1 mole % aq. (187); b.p.  $65.15^\circ$  at 760 mm. contg. 53.8 mole %  $\bar{C}$  + 18.7 mole % allyl alc. + 27.5 mole % aq. (175). —  $\bar{C}$  + *ter*-BuOH (1:0140) + aq: this system forms a const.-boilg. mixt., b.p.  $64.7^\circ$  at 768 mm., contg. about 85 wt. %  $\bar{C}$  + 11.9 wt. % *ter*-BuOH + 3.1 wt. % aq. (188).

$\bar{C}$  + methyl ethyl ketone (1:5405) + aq: this system gives a const.-boilg. mixt., b.p.  $65.7^\circ$  at 760 mm., contg. 76.9 wt. %  $\bar{C}$  + 20.1 wt. % methyl ethyl ketone + 3.0 wt. % aq. (188); for use of this azeotrope in detn. of water in wood see (195).

### OTHER SELECTED PHYSICAL CHARACTERISTICS OF $\bar{C}$

[For studies of thermal conductivity of  $\bar{C}$  see (196) (197) (198); for studies of heat capacity of  $\bar{C}$  (39) (15) (183) as calcd. from spectroscopic data (199) (200) see indic. refs.; for studies of specific heat of  $\bar{C}$  see (21); for studies of heat of fusion and/or of transition see (39) (15) (36) (86) (157); for studies on ebullioscopic const. of  $\bar{C}$ , viz.,  $4.88^\circ$  (201),  $4.68^\circ$  (202) per mole solute in 1000 g.  $\bar{C}$ , see indic. refs.; for studies on cryoscopic const. of  $\bar{C}$ , viz.,  $29.9^\circ$  (203),  $29.8^\circ$  (204) per mole solute in 1000 g.  $\bar{C}$ , see indic. refs.]

[For studies of adsorption of  $\bar{C}$  on various carbons (205) (206) (207) (208) (209) (210) (211) (212) (213) at low press. (214) (215), animal charcoal (216), wood or coconut charcoal (217) (218) (219) (220) (221) (222) (223) (224), alumina gel (225) (226), silica gel (227) (224) (228), Fe(OH)<sub>3</sub> gel (229) (230), Cr(OH)<sub>3</sub> gel (231), TiO<sub>2</sub> gel (232), or mica (233) see indic. refs.]

### PHYSIOLOGICAL ASPECTS OF $\bar{C}$

$\bar{C}$  (as vapor) does not cause acute poisoning until exposure for 30 min. to concns. of 1000–1500 p.p.m. (234) but constant exposure to concns. above 100 p.p.m. (234) (235) or even 50 p.p.m. (236) will cause serious physiological disturbances. The least concn. of  $\bar{C}$  in air detectable by odor is 71.8 p.p.m. (237). For further studies of toxicity and industrial hygiene of  $\bar{C}$  see (238) (239) (240); for study of comparative toxicity of  $\bar{C}$  and 1,1,2-trichloroethylene (3:5170) see (241).

### USES OF $\bar{C}$

$\bar{C}$  is widely used as solvent, fire extinguisher, fumigant, anthelmintic, etc.; although any detailed survey of these aspects is beyond the scope of this book, a few special uses are cited. [For study of use of  $\bar{C}$  as solvent for ozonization see (24); for use in concn. of HNO<sub>3</sub> (242)

or AcOH (243) or in drying of higher alcs. (244) see indic. refs.; for use of molecular compound (245) of  $\bar{C}$  with rotenone in extraction (245) and detn. (246) (247) (248) of rotenone see indic. refs.]

### DETECTION OR DETERMINATION OF $\bar{C}$

Detection of  $\bar{C}$ . [For detection of  $\bar{C}$  in pres. of  $CHCl_3$  (3:5050) q.v. by methods based on differences in aq. soly. (249), or on solv. power for papaverine HCl (250) or quinine sulfate (251), or on color reactions with pyrocatechol (1:1520) (252) (253),  $\alpha$ -naphthol (1:1500) (254) cf. (255), or 2,7-dihydroxynaphthalene (255) cf. (254) (for further details on last two see at end of text of this compd. under  $\bar{O}$ ), see indic. refs. For review of literature of tests for  $\bar{C}$  see (256).]

Note that  $\bar{C}$  does *not* (251) reduce Fehling soln. [dif. from  $CHCl_3$  (3:5050)].

Determination of  $\bar{C}$ . Methods for the detn. of  $\bar{C}$  are based upon both physical and chemical procedures or combinations of the two.

Physical methods include those based upon adsorption of  $\bar{C}$ , e.g., on activated carbon (257) or silica gel (258); by thermal conductivity of vapor of  $\bar{C}$  (259); by measurement of vapor press. (260); or on interference refractrometry (234).

Chemical methods include those based upon decompn. of  $\bar{C}$  by combustion and/or hydrolysis followed by detn. of HCl or of chloride ion, or those based upon color reactions. [For examples of methods based upon combustion followed by detn. of HCl (261) (262) (263) (264) (265) (266) (267) (268) (269) (for combustion in  $H_2$  see (269)); methods based upon hydrolysis with nlo. alk. (270) (271) (272) or reduction with Na + ethanolamioe (273) (274) followed by detn. of chloride ion; or methods based upon use of color (Fujiwara) reaction with pyridine + alkali (275) (276) (277) (278) see indic. refs.]

### DETECTION OF OTHER COMPOUNDS IN $\bar{C}$

[For studies on removal of  $CHCl_3$  (3:5050) from  $\bar{C}$  by digestion with Fehling soln. at 60–70° for several hrs. (280); on detection in  $\bar{C}$  of  $CS_2$  by addn. of MeOH (1:6120) and formn. of  $CS_2$ /MeOH azeotrope of h.p. 37.1° nt 751 mm. (188) or by use of xanthate reaction (281); on removal of  $CS_2$  from  $\bar{C}$  by use of nlc. hydrazine hydrate (282) see indic. refs.; for detection in  $\bar{C}$  of carbonyl chloride see (283) (284) (285) (286) and also under phosgene (3:5000).]

### PREPARATION OR FORMATION OF $\bar{C}$

The principal methods of prepn. of  $\bar{C}$  are those involving chlorination of  $CS_2$  or of hydrocarbons, but many other procedures have been studied as exemplified below.

From carbon disulfide. [Prepn. of  $\bar{C}$  from  $CS_2$  by action of  $Cl_2$  was first effected (287) by passage through red-hot tube; in subsequent development of this method use of various catalysts has been found to reduce the required temperature. The overall reaction is believed to occur in two stages, viz., (1)  $CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$  and (2)  $CS_2 + 2S_2Cl_2 \rightarrow CCl_4 + 6S$ . The resultant sulfur may be recovered and used again in prepn. of  $CS_2$ .]

[For an extensive account of prepn. of  $\bar{C}$  prior to 1906 see monograph of Margosches (288); for longer summary as of 1938 see (289); for still later patents and articles on use of  $Cl_2$  (290) (291) (292) (293) (294) (295) or various sulfur chlorides (296) (297) (298) (299) see indic. refs.]

[For studies on use of various catalysts, e.g.,  $Br_2$  (300),  $I_2$  (301),  $I_2 + Fe$  (302),  $MoCl_5$  (303),  $SbCl_5$  (304), or  $FeCl_3$  (304), see indic. refs.; note that  $CS_2$  reacts with  $SbCl_5$  even without addn. of  $Cl_2$  to give  $\bar{C}$  (305).]

[Note that in chlorination of  $\text{CS}_2$  with restricted amts.  $\text{Cl}_2$  various intermediate carbon chlorosulfides have been detected (306) (307).]

From methane. The formation of  $\bar{\text{C}}$ , together with  $\text{CH}_3\text{Cl}$  (3:7003),  $\text{CH}_2\text{Cl}_2$  (3:5020),  $\text{CHCl}_3$  (3:5050), and other products, has been very extensively studied from many viewpoints. The literature of this reaction is diffuse and interlocked with that of methane and of the various other chlorination products. For this reason and because detailed treatment of this topic is beyond the scope of this book, the following citations must be regarded only as leading references.

[The formn. of  $\bar{\text{C}}$  from  $\text{CH}_4$  by action of  $\text{Cl}_2$  was first discovered in 1840 by Dumas (308). For examples of more recent technical papers ((309)–(317), incl.) and patents ((318)–(332), incl.) see indic. refs.]

From other hydrocarbons. [For examples of patents on prepn. of  $\bar{\text{C}}$  from aliph. hydrocarbons higher than methane (including in some cases also their halogen derivatives) see (313) (333) (334) (335) (336) (337). — For prepn. of  $\bar{\text{C}}$  from acetylene +  $\text{Cl}_2$  + cat. nt 100–200° (338) or with  $\text{Cl}_2$  + eutectic of  $\text{AlCl}_3/\text{NaCl}/\text{FeCl}_3$  at 175–200° (339) see indic. refs. (see also below under prepn. of  $\bar{\text{C}}$  from tetrachloroethylene). — For prepn. of  $\bar{\text{C}}$  from naphthalene by destructive chlorination see (340).]

From various chloro and polychloro compounds. [For technical papers on prepn. of  $\bar{\text{C}}$  from chlorinolysis of various chloro and polychloroparaffins (341) or chloropentanes (342) see indic. refs.]

[For patents on prepn. of  $\bar{\text{C}}$  from tetrachloroethylene (3:5460) with  $\text{Cl}_2$  nt 700–800° (343) or with  $\text{Cl}_2$  over activated carbon at 600–650° (337) see indic. refs.; for study of this reaction see (344). For formn. of  $\bar{\text{C}}$  from hexachloroethane (3:4835) pyrolyzed in air at 550–600° see (342).]

[For prepn. of  $\bar{\text{C}}$  from  $\text{CHCl}_3$  (3:5050) by chlorination with  $\text{Cl}_2$  in sunlight (first prepn. of  $\bar{\text{C}}$ ) (345) or u.v. light (346) (347) (348) (349), nt 260–300° (350), or in pres. of  $\text{FeCl}_3$  (351) or of nq. (352), or from  $\text{CHCl}_3$  with  $\text{ICl}$  at 165° (353), or with  $\text{NaOCl}$  (reaction very slow and incomplete (354)), see indic. refs.]

[For formn. of  $\bar{\text{C}}$  from  $\text{CFCl}_3$  with  $\text{AlCl}_3$  see (355); from  $\text{CBrCl}_3$  with  $\text{Cl}_2$  in dark at 100° (356) or in light (357) (358) see indic. refs.]

From miscellaneous sources. [For formn. of  $\bar{\text{C}}$  from charcoal or other form of carbon +  $\text{Cl}_2$  see patents (359) (361) and technical papers (344) (360); from trichloroacetyl chloride (3:5420) on htg. with  $\text{AlCl}_3$  (362) or pyrolysis through glass tube at 600° (363), from trichloromethyl chloroformate (3:5515) on htg. with  $\text{AlCl}_3$  (364), from chloral (3:5210) with  $\text{Cl}_2$  in sunlight (365), or from acetone (1:5400) with  $\text{NaOCl}$  soln. (366) cf. (354), or from phosgene (3:5000) on htg. with cat. (344) cf. (372), see indic. refs.]

[For formn. of  $\bar{\text{C}}$  from dimethyl sulfide [Beil. I-238, I<sub>1</sub>-(144), I<sub>7</sub>-(276)] with  $\text{Cl}_2$  +  $\text{I}_2$  at 100–120° in daylight see (367) (368) (369); from trichloromethyl sulfur chloride ("perchloromethyl mercaptan") [Beil. III-135, III<sub>1</sub>-(63), III<sub>2</sub>-(106)] on htg. with Fe filings or  $\text{ZnF}_2$  (370) cf. (307) (371) or with  $\text{Cl}_2$  +  $\text{I}_2$  in sunlight (370) see indic. refs.; from thiophosgene [Beil. III-134, III<sub>1</sub>-(63), III<sub>2</sub>-(105)] with Fe nt 37° for many months or from "trichloromethyl dithiochloroformate" [Beil. III-215, III<sub>2</sub>-(155)] with Fe in s.t. at 100° see (307).]

### CHEMICAL BEHAVIOR OF $\bar{\text{C}}$

Pyrolysis of  $\bar{\text{C}}$ . [ $\bar{\text{C}}$  on pyrolysis at 600–1500° (373) (374) cf. (344) (375) (376) gives tetrachloroethylene (3:5460) (80% yield (374)), hexachloroethane (3:4835), and other products.  $\bar{\text{C}}$  by action of electric arc (377) cf. (378), dark electric discharge (in  $\text{H}_2$ ) (379), radium emanation (350), gives hexachloroethane (3:4835) and various other products.]

[Note also that  $\bar{C}$  in X-radiation (381) (382) or ultrasonic radiation (383) splits off some  $Cl_2$ . For action of X-radiation on mixts. of  $\bar{C}$  with aq.,  $CHCl_3$ ,  $CHI_3$ , lgr., or cyclohexane see (381) (384); for decompn. of  $\bar{C}$  in u.v. light below 2750 Å see (385).]

**Oxidation of  $\bar{C}$ .**  $\bar{C}$  under various oxidizing conditions yields phosgene and other products. [E.g.,  $\bar{C}$  with  $O_2$  in light of 2537 Å (386) or with atomic oxygen (387) gives carbonyl chloride (3:5000);  $\bar{C}$  with  $O_2$  over white-hot Pt (375), or with air over  $CuCl_2$  or  $FeCl_3$  at elev. temp. (388), or  $\bar{C}$  over  $GeO_2$  (389), or  $\bar{C}$  with pyrosulfuryl chloride (1 mole) + sulfuric acid monohydrate (2 moles) on warming (390) (391) (392) (393) gives phosgene (3:5000). For formn. of phosgene (3:5000) q.v. during thermal decompn. of  $\bar{C}$  (as in use as fire extinguisher) see (394), also below under behavior of  $\bar{C}$  with metals.] [Note that  $\bar{C}$ , unlike  $CHCl_3$  (3:5050), is *not* oxidized by Fehling soln.]

**Reduction of  $\bar{C}$ .** [ $\bar{C}$  with  $K/Hg$  + aq. gives (395) methane;  $\bar{C}$  with  $Fe(OH)_2$  + aq. alk. gives (396)  $CH_2Cl_2$  (3:5020) +  $CHCl_3$  (3:5050);  $\bar{C}$  with  $Zn$  +  $H_2SO_4$  (397) (398), finely divided  $Fe$  + aq. (399) + cat. (400) (401), or on electrolytic reduction (402) gives  $CHCl_3$  (3:5050). For behavior of  $\bar{C}$  with atomic hydrogen see (403).]

[Note that  $\bar{C}$  +  $H_2$  over pumice in hot tube gives (404)  $CHCl_3$  (3:5050),  $CH_2Cl_2$  (3:5020), tetrachloroethylene (3:5460) + hexachloroethane (3:4835), and at red heat (395) methane and ethylene.  $\bar{C}$  with excess  $H_2$  over reduced  $Ni$  at 270° gives (405) hexachloroethane (3:4835) +  $HCl$ .]

**Substitution of  $\bar{C}$ .**  $\bar{C}$  by reaction with  $F_2$ , metallic fluorides, or  $HF$ , etc., each in the presence of appropriate catalysts, undergoes replacement of one or more of its chlorine atoms by fluorine and consequent formation of mixed derivatives such as  $CCl_3F$ ,  $CCl_2F_2$  ("Freon" = "Freon-12" "F-12"),  $CClF_3$ , etc., to whose properties as refrigerants, etc., much attention is currently being given. [Detailed analysis of the conversion of  $\bar{C}$  to these materials is far beyond the scope of this book, but for examples of leading technical papers (406) (407) (408) (409) (410) (411) and patents ((412)-(429)) see indic. refs.] (See also below under behavior of  $\bar{C}$  with inorganic salts.)

**Hydrolysis of  $\bar{C}$ .** [ $\bar{C}$  with aq. on long exposure (e.g., 7 months (430)) to sunlight gives  $CO_2$  +  $HCl$ ;  $\bar{C}$  with large excess of aq. in s.t. at 250° also gives  $CO_2$  +  $HCl$ , but  $\bar{C}$  with very small proportion of aq. under same conditions gives (431) some phosgene (3:5000). At ord. temp. hydrolysis of  $\bar{C}$  by pure aq. is scarcely perceptible, but in presence of  $Fe$ ,  $Cu$ , acid, or alkali, hydrolysis is strongly accelerated especially at higher temperatures (432).  $\bar{C}$  is hydrolyzed by aq. + reduced  $Fe$  but not by aq.  $NaHCO_3$  (342) under reflux.]

[ $\bar{C}$  with boilg. alc. alk. is eventually completely hydrolyzed (use in detn. of  $\bar{C}$  by estimation of resultant chloride ion (see above)); however, reaction is slow and with  $N$  aq. or alc.  $KOH$  or  $NaOEt$  at 60° is very slight in 2 hrs. (433). For study of rate of hydrolysis of  $\bar{C}$  with  $KOH$  in 95% alc. (434) cf. (435), or with  $Ba(OH)_2$  or  $TiOH$  in 50% alc. (436), see indic. refs.]

**Behavior of  $\bar{C}$  with inorganic salts.** [ $\bar{C}$  with  $AlBr_3$  at room temp. for 3 days gives (358)  $CBrCl_3$  [Beil. I-67, I<sub>2</sub>-(31)], b.p. 104.2-104.35° at 758.5 mm. (358), but  $\bar{C}$  with  $AlBr_3$  at 60° gives (437) cf. (438)  $CBr_4$  [Beil. I-68, I<sub>1</sub>-(17), I<sub>2</sub>-(35)], m.p. 94°, b.p. 189.5° at 760 mm. with slight decompn. (439).]

[ $\bar{C}$  with  $AlI_3$  (440),  $Al$  +  $I_2$  in  $CS_2$  (441),  $CaI_2$  +  $2H_2O$  or  $LiI$  +  $1.5H_2O$  in evacuated s.t. at 90-92° for 5 days (50-55% yield (442)) (443), with  $BI_3$  (444), or  $\bar{C}$  (1 mole) +  $C_2H_5I$  (4 moles) +  $AlCl_3$  (0.1 mole) (445), or best  $\bar{C}$  (0.7 mole) with  $CH_3I$  (2.94 moles) +  $AlCl_3$  (0.015 mole) at 40° (92% yield (446)) gives carbon tetraiodide,  $CI_4$  [Beil. I-74, I<sub>1</sub>-(19), I<sub>2</sub>-(39)].]

$\bar{C}$  with alc.  $AgNO_3$  does not react even after several days; note that in this respect  $\bar{C}$  behaves like  $CH_2Cl_2$  (3:5020) and  $CHCl_3$  (3:5050) while  $CH_3Cl$  (3:7005) gives a ppt. within 3 hrs. (446).

Behavior of  $\bar{C}$  with metals.  $\bar{C}$  with alkali or even alkaline-earth metals undergoes explosive decompn. on htg. or even at room temp. if subjected to sufficient mechanical shock. [For studies on the explosion of  $\bar{C}$  with alkali metals see (477) (448); for further studies on explosion of  $\bar{C}$  with Li, Na, K, Ca, Sr, Ba, Mg, Al, and Tl, especially with reference to sensitivity to mechanical shock, see (449). — For behavior of  $\bar{C}$  with Na vapor see (450); for rate of reaction of  $\bar{C}$  with Na atoms see (451); for study of  $\bar{C}$  + Na/Hg as means of sepn. of isotopes of chlorine see (452) cf. (453).]

[For study of hazards of behavior of  $CCl_4/CHCl_3$  mixts. with Mg (454) (455) or Al (454) see indic. refs., note also that  $\bar{C}$  refluxed with Al powder (456) or Al/Hg (457), or  $\bar{C}$  with Al +  $AlCl_3$  at 60–75° (458), or  $\bar{C}$  with Cu powder at 120° (458) or molecular Ag at 200° (431) gives (yields. 80% (456), 65% (457)) hexachloroethane (3:4835).]

Note that  $\bar{C}$  with Mg in boilg. ether does not react, even in the presence of various catalysts (459).

[For extensive study of corrosion of metals by  $\bar{C}$  (460) cf. (461) (462) (463) (432) see indic. refs.]

Behavior of  $\bar{C}$  with other inorganic reactants. [ $\bar{C}$  is claimed to be unaffected by conc.  $H_2SO_4$  at 237° (464) although over  $H_2SO_4$  on pumice at 150°  $\bar{C}$  is reported (465) to give  $HCl$ ,  $SO_2$ ,  $COCl_2$  +  $CO_2$ ]

[For study of photochem. reaction of  $\bar{C}$  with  $H_2S$  giving hexachloroethane (3:4835) + S +  $CCl_3SH$  see (466); for studies on photochem. decompn. of  $Cl_2O$  in  $\bar{C}$  see (467) (468) (469) (470) cf. (471); for behavior of  $\bar{C}$  with  $Br_2O$  giving phosgene (3:5000) +  $Cl_2$  +  $Br_2$  see (472).]

[ $\bar{C}$  with  $NH_3$  under high press. in pres. of Cu +  $I_2$  at 140° for 17 hrs. gives (35–40% yield (473)) guanidine hydrochloride [Beil. III 82, III<sub>1</sub>-(39), III<sub>2</sub>-(69)]. —  $\bar{C}$  with hydrazine hydrate in stream of  $NH_3$  refluxed for several days gives (poor yield (474))  $N,N',N''$ -triaminoguanidine [Beil. III-122, III<sub>1</sub>-(57), III<sub>2</sub>-(97)], as monohydrochloride, m.p. 228° dec.]

Behavior of  $\bar{C}$  with organic reactants. With carbon monoxide. [ $\bar{C}$  with CO +  $AlCl_3$  at 200° and 250 atm for 6 hrs gives (37% yield (475)) trichloroacetyl chloride (3:5420).]

With hydrocarbons. [ $\bar{C}$  (excess) with octene-1 (1:8375) in pres. of small amts. (0.02 mole) of dibenzoyl peroxide (or diacetyl peroxide) adds to unsatd. linkage giving (476) 1,1,1,3-tetrachlorooctane; under similar conditions  $\bar{C}$  adds to one of the unsatd. linkages of diallyl (1:8045) giving 5,7,7,7-tetrachloroheptene-1 or to both giving 1,1,1,3,6,8,8,8-octachloro-octane. — For other addns of  $\bar{C}$  to olefin linkages see below.]

[ $\bar{C}$  with  $C_6H_6$  in pres. of  $AlCl_3$  gives according to conditions triphenylchloromethane (3:3410) (477), triphenylmethane (1:7220) (478), or benzophenone (1:5150) (479). Other arom. hydrocarbons and aryl halides behave similarly but cannot be detailed here.]

With saturated halohydrocarbons.  $\bar{C}$  (0.7 mole) with MeI (2.94 moles) +  $AlCl_3$  (0.015 mole) at 40° gives (92% yield (446)) carbon tetraiodide (see also above under behavior of  $\bar{C}$  with inorganic salts). —  $\bar{C}$  with  $CBr_4$  in pres. of slightly moistened  $AlCl_3$  at 170° for 7 hrs. undergoes a redistribution reaction giving (480) an equil. mixt. of  $CCl_4$ ,  $CCl_3Br$ ,  $CCl_2Br_2$ ,  $CClBr_3$ , and  $CBr_4$ ]

With unsaturated halohydrocarbons. [ $\bar{C}$  with ord. 1,2-dichloroethylene (3:5030) +  $AlCl_3$  gives (481) (482) cf. (483) 1,1,1,2,3,3,3-heptachloropropane (3:6460); for reaction of this system yielding heptachloropentenes see (483).]

[ $\bar{C}$  with trichloroethylene (3:5170) +  $AlCl_3$  at 20–30° for 48 hrs. gives (49% yield (484)) (481) (482) 1,1,1,2,3,3,3-heptachloropropane (3:6560).]

With alcohols or alcoholates. [ $\bar{C}$  with MeOH over cat. at 200–350° gives (485) MeCl (3:7005);  $\bar{C}$  with EtOH under similar circumstances gives EtCl (3:7015).]

[ $\bar{C}$  with  $NaOCH_3$  would be expected to yield tetramethyl orthocarbonate [Beil. III<sub>2</sub>-(4)],

h.p. 112–113° at 724 mm. (486),  $n_D^{12} = 1.3841$  (486), but this reaction is unreported, the expected prod. having been made only by other methods. —  $\bar{C}$  with  $\text{NaOC}_2\text{H}_5$  would be expected to yield tetraethyl orthocarbonate [Beil. III-5, III<sub>1</sub>-(4), III<sub>2</sub>-(5)], h.p. 157–158° (487), 59.6–60° at 14 mm. (486),  $D_4^{18.5} = 0.9197$  (488),  $n_D^{18.5} = 1.39354$  (488), but this reaction is unreported cf. (505); however, the prod. has been prepd. from  $\text{CBr}_4$  with  $\text{NaOEt}$  in dry ether in s.t. at 170° (457), from "thiocarbonyl tetrachloride,"  $\text{CSCl}_4$  cf. (459) refluxed in dry ether with  $\text{NaOEt}$ , and in other ways.]

*With mercaptans or mercaptides.* [ $\bar{C}$  with  $\text{NaSCH}_3$  might be expected to give tetramethyl tetrathioorthocarbonate,  $\text{C}(\text{SCH}_3)_4$ , but this appears to be unreported;  $\bar{C}$  with  $\text{NaSCH}_3$  has been found (492) to react differently giving trimethyl trithioorthoformate [Beil. II<sub>7</sub>-(39)], m.p. 16° (493), h.p. 220° dec. (493), 103–104° at 12 mm. (492), 96° at 9 mm. (493),  $n_D^{15} = 1.5696$  (492), and dimethyl disulfide, b.p. 39–41° at 18 mm. (492). —  $\bar{C}$  with  $\text{NaSC}_2\text{H}_5$  is claimed (491) to give the expected homologous tetraethyl tetrathioorthocarbonate  $\text{C}(\text{SC}_2\text{H}_5)_4$ , but this material was not well characterized, and  $\bar{C}$  with  $\text{NaSC}_2\text{H}_5$  has subsequently (492) been found to give triethyl trithioorthoformate [Beil. II-95, II<sub>7</sub>-(39)], b.p. 235° dec. (493), 174° at 760 mm. (494),  $D_4^{20} = 1.053$  (495),  $n_D^{15} = 1.5410$  (492). — For behavior of  $\bar{C}$  with salts of *n*-propyl, *n*-butyl, and *ter*-butyl mercaptans see (492).]

*With phenols or phenolates.* [ $\bar{C}$  with phenol (1:1420) in pres. of  $\text{ZnCl}_2 + \text{ZnO}$  at 120° gives (496) diphenyl carbonate (1:2335), various dihydroxybenzophenones, and other products; for analogous study of  $\bar{C}$  with *o*-cresol (1:1400) see (497).]

[ $\bar{C}$  with *K* phenolate at 170° gives mainly (498) aurin (paraosolic acid) (4'-4''-dihydroxy-fuchson) [Beil. VIII-361, VIII<sub>1</sub>-(671)]; for analogous behavior of  $\bar{C}$  with *K o*-cresolate and *K m*-cresolate see (498).]

*With diacyl peroxides.* [ $\bar{C}$  refluxed with di-*n*-butyryl peroxide for 17 hrs. gives (499) *n*-propyl chloride (3:7040) + hexachloroethane (3:4835) + ethyl *n*-butyrate (1:3127);  $\bar{C}$  refluxed similarly with di-*n*-isobutyryl peroxide gives (499) isopropyl chloride (3:7025) + hexachloroethane (3:4835) + ethyl isobutyrate (1:3095).]

[ $\bar{C}$  with di- $\alpha$ -naphthyl peroxide under reflux gives (500)  $\text{CO}_2$ ,  $\alpha$ -chloronaphthalene (3:6878),  $\alpha$ -naphthoic acid (1:0785), and other products;  $\bar{C}$  with di- $\beta$ -naphthyl peroxide under reflux gives (500)  $\text{CO}_2$ ,  $\beta$ -chloronaphthalene (3:1285),  $\beta$ -naphthoic acid (1:0800), and other products.]

[ $\bar{C}$  with dibenzoyl peroxide under reflux gives (501) (502) (503) 4-(trichloromethyl)-benzoic acid, hexachloroethane (3:4835), phosgene (3:5000), chlorobenzene (3:7903), and other products; for study of kinetics of reaction see (504).]

*With salts of enolic esters.* [ $\bar{C}$  with diethyl sodio-malonate (505) (507) or with diethyl disodio-malonate (506) (507) (508) (509) gives the Na enolate of tetraethyl  $\alpha,\gamma$ -dicarboxy-glutaconate,  $(\text{C}_2\text{H}_5\text{OOC})_2\text{C}=\text{CH}-\text{CH}(\text{COOC}_2\text{H}_5)_2$  [Beil. II-876, II<sub>7</sub>-(336), II<sub>7</sub>-(710)], h.p. 208–210° at 23 mm. (510), 200–204° at 18 mm. (510); note that this product is also obtd. from  $\text{CHCl}_3$  (3:5050) with diethyl sodio-malonate (505) (511) (512) (513) (514) (515) (516) (517).]

[ $\bar{C}$  with 4 moles of Na enolate of ethyl cyanoacetate in alc. at 100° gives (505) cf. (508) the sodium enolate of diethyl  $\alpha,\gamma$ -dicyanoglutaconate,  $\text{C}_2\text{H}_5\text{OOC}-\text{C}(\text{CN})=\text{CH}-\text{CH}(\text{CN})\text{COOC}_2\text{H}_5$  [Beil. II-878, II<sub>7</sub>-(712)], also obtd. from  $\text{CHCl}_3$  (3:5050) with the Na enolate of ethyl cyanoacetate (518) (519) (520).]

*With amines.* The behavior of  $\bar{C}$  with amines has been little studied. [For studies on the behavior of  $\bar{C}$  with aniline (521) and also with other aromatic amines in pres. of Cu powder (522) or  $\text{I}_2$  (523) see indic. refs.]

Ⓔ Color reaction with  $\alpha$ -naphthol/cyclohexanol.  $\bar{C}$  (1 drop) with 2 mL of a 2% soln. of  $\alpha$ -naphthol (1:1500) in cyclohexanol (1:6415) + 1 pellet of solid NaOH, boiled

25 seconds and cooled, gives (254) blue color; one portion of this blue solution under-laid with equal volume 85%  $H_2SO_4$ , stood 1 min and shaken, remains blue; a second portion of the alkaline blue soln. acidified with equal vol.  $AcOH$  (1:1010), stood 1 min. and shaken, becomes red. [Note that the alkaline boilg. also gives a blue color with  $CH_2Cl_2$  (3.5020) and with  $CHCl_3$  (3.5050), while other chlorinated solvents (254) give yellow-brown, gray, or brown; in the  $H_2SO_4$  acidification  $CH_2Cl_2$  (3.5020) gives greenish blue, while both  $CHCl_3$  (3.5050) and  $\bar{C}$  give intense blue; in the  $AcOH$  acidification  $CH_2Cl_2$  (3.5020) gives yellow while  $CHCl_3$  (3.5050) gives an orange-yellow color]

③ Color test with 2,7-dihydroxynaphthalene/cyclohexanol.  $\bar{C}$  (1 drop) with 2 ml. pure cyclohexanol (1.6415) + 1 pellet  $NaOH$  + a few mgms 2,7-dihydroxynaphthalene htd at  $197^\circ$  (b.p. of ethylene glycol) for 45 seconds, decanted from undissolved  $NaOH$ , cooled, and shaken with 2 ml.  $AcOH$  + 4 ml 96%  $EtOH$ , gives a pale yellow-brown color (255). [Note that under these conditions  $CH_2Cl_2$  (3.5020) gives a steel-blue color while  $CHCl_3$  (3.5050) gives a deep red color.]

④ Color test with cyclopentanol.  $\bar{C}$  (1 drop) in 1 ml. cyclopentanol (1.6412) + 1 pellet  $NaOH$  boiled 25 seconds, then shaken vigorously for 35 seconds, and treated with 4 ml. 96%  $EtOH$  and shaken, gives an intense brown color (255) [Note that, after addition of alc.,  $CH_2Cl_2$  (3.5020) gives a more intense red or becomes reddish brown while  $CHCl_3$  (3.5050) gives only a pale citron-yellow. By comparing with authentic known samples, this test is claimed (255) to be able to detect as little as 5%  $\bar{C}$  in  $CHCl_3$ .]

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3:5110 1,2-DICHLOROPROPENE-1  $\text{CH}_3-\text{C}=\text{CH}$   $\text{C}_3\text{H}_4\text{Cl}_2$  Bell. I - 199  
(Low-boilg. stereoisomer)  $\begin{array}{c} \text{Cl} \quad \text{Cl} \\ | \quad | \end{array}$   $\begin{array}{c} \text{I}_1- \\ \text{I}_2- \end{array}$

B.P.

77.0° at 767.2 mm. (1)

75° (2)

$D_4^{25} = 1.1755$  (1)  $n_D^{25} = 1.4451$  (1)

$D_4^{20} = 1.1818$  (1)  $n_D^{20} = 1.4471$  (1)

[See also the higher-boilg. stereoisomer (3:5150).]

[For prepn. of  $\bar{\text{C}}$  from 1,2,2-trichloropropane (3:5475) with MeOH/NaOMe or EtOH NaOEt at ord. temp. (55-58% yield (1)), or with alc. KOH (2) or with nq. on hgt. in s.l. (3), see indie. refs.]

$\bar{\text{C}}$  with abs. MeOH (1:6120) forms a const.-boilg. mixt., b.p. 50.5-50.8° at 760 mm.,  $n_D^{25} = 1.4030$ , contg. 75 wt. %  $\bar{\text{C}}$  (1).

$\bar{\text{C}}$  with  $\text{Cl}_2$  at 0° in strong light adds 1 mole halogen giving (1) 1,1,2,2-tetrachloropropane (3:5825).

$\bar{C}$  with  $Br_2$  at  $0^\circ$  slowly adds 1 mole halogen giving (1) (3) 1,2-dibromo-1,2-dichloropropane, b.p.  $190^\circ$  (3).

$\bar{C}$  with  $O_3$  in  $CCl_4$  at  $-15^\circ$  followed by aq. gives (1) acetic acid (1:1010) and formic acid (1:1005).

3:5110 (1) Huntress, Sanchez-Nieva, unpublished work. (2) Friedel, Silva, *Bull. soc. chim.* (2) 17, 386 (1872); *Jahresber.* 1872, 322, *Compt. rend.* 74, 805-809 (1872); 75, 81-85 (1872). (3) Friedel, Silva, *Jahresber.* 1871, 322, 329.

3:5120 1,1-DICHLOROPROPENE-1  $CH_2CH=CCl_2$   $C_3H_4Cl_2$  Beil. 1-199

 $I_1-$ 
 $I_2-$ 

B.P.  $79-80^\circ$  (1)  
 $78^\circ$  (2) (3) (4) (5)  
 $77.15-77.35$  (6)  
 $77^\circ$  (7)  
 $76.5^\circ$  (8)

$D_0^{19.5} = 1.1764$  (8)  
 $D_0^0 = 1.2030$  (8)

Colorless oil insol. in aq.

[For prepn. of  $\bar{C}$  from 1,1,1-trichloropropanol-2 (3:0846) with Zn dust + AcOH see (6) (5); from corresp. acetate with Zn dust + alc. see (8); from butylchloral ( $\alpha,\alpha,\beta$ -trichloro-*n*-butyraldehyde) (3:5910) (1) (2) (9) or its alcoholate (10) with KOH see indic. refs.; from Ag 2,2,3-trichlorobutyrate on boilg. with aq. (3) or Na 2,2,3-trichlorobutyrate on distn. (4) see (3) (4); for prepn. from 1,1,2-trichloropropane (3:5630) + aq. or alc. alk. or aq.  $Ca(OH)_2$  see (11) (14).]

$\bar{C}$  on oxidn. with  $K_2Cr_2O_7 + H_2SO_4$  gives (7) AcOH (1:1010).

$\bar{C}$  adds  $Br_2$  very easily giving (9) 1,1-dichloro-1,2-dibromopropane [Beil. I-111], b.p.  $188^\circ$  (9). —  $\bar{C}$  with  $Cl_2$  at  $0-30^\circ$  yields (12) 1,1,1,2-tetrachloropropane (3:5270), b.p.  $153^\circ$ .

$\bar{C}$  with  $HCl + AlCl_3$  at  $5-10^\circ$  yields (13) (14) 1,1,1-trichloropropane (ethylchloroform) (3:5270), b.p.  $106-107^\circ$ .

3:5120 (1) Krämer, Pinner, *Ber.* 3, 388-389 (1870). (2) Krämer, Pinner, *Ann.* 158, 47-49 (1871). (3) Judson, *Ber.* 3, 789 (1870). (4) Valentini, *Ber.* 28, 2663 (1895). (5) Wohl, Roth, *Ber.* 40, 215 (1907). (6) Bruyne, Davis, Gross, *Physik Z.* 33, 720 (1932). (7) Lieben, Zeisel, *Monatsh.* 4, 536 (1883). (8) Faworski, Jozitsch, *J. Russ. Phys.-Chem. Soc.* 30, 998-1003 (1898); *Cent.* 1899, I 778. (9) Pinner, *Ann.* 179, 44-45 (1875). (10) Freundler, *Bull. soc. chim.* (4) 1, 501-503 (1907).

(11) Cass (to du Pont), U.S. 2,134,102, Oct. 25, 1938; *Brit.* 471,186, Sept. 30, 1937. (12) Cass (to du Pont) U.S. 2,097,442, Nov. 2, 1937; *Brit.* 471,187, Sept. 30, 1937; *Cent.* 1938, 1218. (13) Levine, Cass (to du Pont), U.S. 2,179,215, Nov. 7, 1939; *Brit.* 503,015, May 11, 1939; *Cent.* 1939, II 1572. (14) Henne, Whaley, *J. Am. Chem. Soc.* 64, 1157 (1942).



3:5130 1,2-DICHLOROETHANE  
(Ethylene (di)chloride;  
*sym.*-dichloroethane)



Beil. I - 84  
I<sub>1</sub>-(24)  
I<sub>2</sub>-(52)

B.P.	F.P.			
84.1° cor. at 760 mm. (1)	[-32.5° (2S)]	$D_4^{25} = 1.2525$	(40)	$n_D^{25} = 1.4430$ (47)
84.08°	-35.3° (35)	1.2463	(41)	1.4427 (91)
cor. at 760 mm. (2)				
84° at 760 mm. (3)	36° (11)	1.24571	(44)	1.4423 (14)
83.9° at 766 mm. (4)	-35.5° (23)	1.24554	(23)	1.44118 (48)
83.8° (5) (6)	(5)	1.2455	(42)	
83.75° at 760 mm. (7)	-35.8° (24)	1.2445	(43)	
83.7-84.3° (8)	-35.9° (37)	1.2444	(4)	
83.7-83.9°	-36.0° (34)			
cor. at 772 mm. (9)	(3S)			
83.7° at 760 mm. (10)		$D_4^{20} = 1.2569$	(10)	$n_D^{20} = 1.44507$ (49)
(11) (12) (111) (112)	[-42.0° (39)]		(22) (34)	1.44505 (50)
83.65-83.70° at 760 mm. (13)		1.2541	(12)	1.44476 (18)
83.65° at 760 mm. (14)		1.25295	(44)	(19) (20)
83.6-83.8° (15) (16) (17)		1.25277	(23)	1.4447 (51)
83.5-83.7° (18) (19) (20)		1.2521	(45)	1.4446 (52)
83.5° at 760 mm. (21)		1.252	(3)	(79)
(22) (23) (34)		1.2515	(4)	1.4444 (53)
83.5° (24)		1.2501	(46)	1.44439 (46)
83.481° cor. at 760 mm. (25)				1.44432 (45)
83.45° at 760 mm. (26)				1.4443 (201)
83.43-83.48° (27)				1.4440 (54)
83.4-83.6° (28)				1.444 (34)
83.3° at 749 mm. (29)				1.44268 (13)
83° (30)				
82.85° at 760 mm. (100)		$D_4^{15} = 1.26000$	(23)	$n_D^{15} = 1.44759$ (23)
82.6-82.8° at 743 mm. (31)				See note 3.
82.4° at 747 mm. (32)				
82.3-82.6° (33)				
81.47° cor. at 700 mm. (2)				
79.325° cor. at 660.8 mm. (25)				
76.63° cor. at 600 mm. (2)				
75.05° cor. at 500 mm. (2)				
64.73° cor. at 400 mm. (2)				

See also Notes 1 and 2.

Note 1. For b.p. of  $\bar{C}$  at press. 660-860 mm. (25), 400-1080 mm. (2), see indic. refs.;  $\bar{C}$  has b.p. 84.9-85.5° at 777 mm. (53).

Note 2. For vap. press. of  $\bar{C}$  over range -30 to 100° (1), or 0-30° (8), or 0-25° (55) see indic. refs.; for relation between vap. press. and temp. see (56) (25).

Note 3. For values of  $n^{18.4}$  at 14 different wave lengths see (57).

Care must be taken to avoid confusion of  $\bar{C}$  with either *cis* (3:5042) or *trans* (3:5028) 1,2-dichloroethylene.

## MISCELLANEOUS PHYSICAL PROPERTIES

Various solubility relations.  $\bar{C}$  is almost insol. aq., but easily volatile with steam (see under azeotropes); soly. of  $\bar{C}$  in 100 g. aq. at  $0^\circ$  is 0.873 g. {58}, 0.922 g. {8}; at  $10^\circ$  = 0.885 g. {8}; at  $15^\circ$  = 0.872 g. {59}, at  $20^\circ$  = 0.869 g. {8}, 0.849 g. {58}; at  $25^\circ$  = 0.865 g. {15}; at  $30^\circ$  = 0.90 g. {59}, 0.894 g. {8}; at  $35^\circ$  = 0.895 g. {58}; at  $56^\circ$  = 1.030 g. {58}. — [For influence of added salts in diminishing soly. of  $\bar{C}$  in aq. see {16}. — Note that  $\bar{C}$  with aq. under press. forms a solid hydrate which can be maintained up to  $+18^\circ$  under 100 atm. but which at ord. press. decomposes below  $0^\circ$  {60}. — For soly. of aq. in  $\bar{C}$  at  $0^\circ$ ,  $25^\circ$ , and  $30^\circ$  (as detd. by Karl Fischer reagent.) see {61}.]

[For soly. in  $\bar{C}$  of  $\text{NH}_3$  at  $20^\circ$  and 1 atm. {62}, of  $\text{H}_2\text{S}$  at  $20^\circ$  and 1 atm. {62}, of  $\text{HCl}$  at various temps. and press. {62} {63}, of ethylene at  $0-40^\circ$  {4}, or of chlorine at  $-9^\circ$  to  $+40^\circ$  {4} see indic. refs.]

[For soly. in  $\bar{C}$  of  $\text{I}_2$  over range  $11-25^\circ$  (and comparison with other chlorinated solvents) see {64}.]

[For study of industrial recovery of  $\bar{C}$  by countercurrent absorption in kerosene see {65}.]

Adsorption of  $\bar{C}$  by solids. [For studies on adsorption of  $\bar{C}$  by activated carbon {66} {67} {68} {69} {70}, by silica gel {67}, or by alumina gel {71} see indic. refs. — For patent on sepn. of  $\bar{C}$  from nther solvents by adsorption on carbon see {72}.]

Other properties. [For study of thermal conductivity of  $\bar{C}$  see {73}; for study of diffusion of vapors of  $\bar{C}$  through films of various cellulose esters see {74}.]

Binary systems contg.  $\bar{C}$ . (See also azeotropes (below).)

$\bar{C}$  with hydrocarbons —  $\bar{C}$  + *n*-heptane (1:8575): use in testing of distg. columns (detn. of number of theoret. plates) see {75}. —  $\bar{C}$  + cyclohexane (1:8405): for values of  $D_0^{20}$  and  $n_D^{20}$  {49}, for use in detn. of number of theoret. plates in distg. columns {75}, or for sepn. of  $\bar{C}$  from system by forming azeotrope of cyclohexane with  $\text{MeOH}$  {76}, see indic. refs. (see also below under azeotropes).

$\bar{C}$  + benzene (1:7400): note that because of the proximity of the b.p.'s of the components, because of the importance of both as industrial solvents, and because they are not readily separable by chemical means (such as  $\text{H}_2\text{SO}_4$ , etc.) a great deal of study has been given to the system from various viewpoints.

For l.p./compn. data on system  $\bar{C}$  +  $\text{C}_6\text{H}_6$ , eutectic, f.p.  $-54.2^\circ$ , contg. about 67 mole %  $\bar{C}$  see {24} cf. {77}; for  $D_0^{20}$  {78} {79},  $n_D^{20}$  {78} {79} {49}, or  $n_D^{25.2}$  {80} {89} cf. {81} see indic. refs. — For use of this system as test liq. for studying efficiency of distn. columns see {81} {78} {79} {82}, for study of distn. of the system see {78} {79} {81} {82} {83} {84} {85}; for use in detn. number of theoret. plates see {75} {78}; for data on vap. press. of system, vapor liq. compn., etc., see {86} {87} {88} {80} {49} {89} {90}.

$\bar{C}$  + toluene (1:7105): for  $n_D^{20}$  for system see {91} {92}; for vapor-liq. equil. data and study of distn. of system see {83} {91} {92} {93}.

$\bar{C}$  with other cpds. of Order I.  $\bar{C}$  + acetic acid (1:1010): for values of  $D$  and  $n$  for the system see {94}, for vapor-liq. equil. see {95}; see also under values of  $\bar{C}$  (below). —  $\bar{C}$  + phenol (1:1420): for vap. press. of system see {96}. —  $\bar{C}$  + acetone (1:5400): for  $D$  and  $n_D^{20}$  see {49} {94}, for vapor-liquid equil. see {49}. —  $\bar{C}$  + diethyl ether (1:6110): for l.p./compn. data and diag. see {21}; for  $D_0^{20}$  over range  $0-40^\circ$  see {97}. —  $\bar{C}$  + ethylene oxide (1:6105): for soly. and vap. press. {98} and vapor-liq. equil. {106} see indic. refs.

$\bar{C}$  with cpds. of Order III.  $\bar{C}$  +  $\text{CHCl}_3$  (3:5050): for b.p./compn. diag. see {93}. —  $\bar{C}$  +  $\text{CCl}_4$  (3:5100): for  $D_0^{20}$  {100} and vapor-liq. compn. data and diagrams {100} {93} {88} (see also below under azeotropes).

$\bar{C}$  + 1,1-dichloroethane (3:5035): for b.p. at 760 mm.,  $D_4^{20}$ , and vapor-liq. equil. data see {101}. —  $\bar{C}$  + 1,1,2-trichloroethane (3:5330): for l.p./compn. data, eutectic f.p.  $-79^\circ$

Note that oxidn. of  $\bar{C}$  with  $CrO_3/H_2SO_4$  in pres. of Hg yields  $CO_2$  quantitatively (196) (dif. from many polychloro cpds.). — Note also that  $\bar{C}$  does not respond to the R + H "Tri-Per Analyzer" (a recording ultra-violet photometer) (197).

For detn. of  $\bar{C}$  in organs and tissues see (198).

### PREPARATION OF $\bar{C}$

The most-studied method for prepn. and manufacture of  $\bar{C}$  is that from ethylene by addn. of chlorine; this method is also of historical interest as leading to the discovery of  $\bar{C}$  in 1795 (199) and its initial designation as "oil of the four Dutch chemists." — Various other modes of formn. of  $\bar{C}$  have since been discovered and will be indicated below.

**Preparation from ethylene. By use of chlorine.** Ethylene with chlorine under certain conditions adds chlorine quant. yielding only  $\bar{C}$ ; under other conditions, however, the system gives 1,1,2-trichloroethane (3:5330) + HCl. — In the absence of catalysts, the substitution reactn. is avoided by use of very low temperatures; in the presence of catalysts addition (rather than substitution) is facilitated even at the higher temperatures (e.g., 120°) resulting from heat of reactn.

For general articles discussing the various factors involved see (200) (201) (53) (202) (203) (204) (205) (69); for articles discussing the reaction from the viewpoint of utilization of the ethylene of industrial gases see (206)–(214) incl.; for patents on prepn. of  $\bar{C}$  from ethylene +  $Cl_2$  see (215)–(236) incl. [For prepn. of "heavy"  $\bar{C}$  contg. one  $C^{13}$  atom see below under miscell. prepn.]

**By use of  $HOCl$  ( $Cl_2 + H_2O$ , etc.).** Although ethylene with  $HOCl$  solns. gives mainly ethylene chlorohydrin (3:5552) nevertheless some  $\bar{C}$  is formed; for studies of this reactn. see (237) (238) (239) (240) (241).

**By other miscellaneous reagents.** [For formn. of  $\bar{C}$  (together with other prods.) from ethylene with  $Cl_2$  in  $AcOH$  or  $Ac_2O$  soln. (242), with  $HCl$  + air over pumice contg.  $CuCl_2$  at 300° (243), with aq.  $ICl$  (244), with  $NCl_3$  in  $CCl_4$  soln. at 20–25° for 7 days (245), with nitryl chloride ( $ClNO_2$ ) (246), with  $SbCl_5$  or  $CuCl_2$  (247), or with *N*-chlorourea (253) see indic. refs.]

**Formation of  $\bar{C}$  from ethane or acetylene.** [For formn. of  $\bar{C}$  from ethane with  $NOCl$  at 300° (248) or with  $Cl_2 + O_2 + cat.$  at 300–650° (249) see indic. refs.; for formn. of  $\bar{C}$  (together with other prods.) from acetylene with  $HCl$  gas in pres. of  $NO_2$  (250), or with  $Cl_2$  in pres. of  $CCl_4 + AlCl_3/NaCl/FeCl_3$  at 175–250° (251) cf. (252), see indic. refs.]

**Formation of  $\bar{C}$  from miscellaneous sources and by various methods.** [For formn. of  $\bar{C}$  (together with other prods.) from methyl chloride (3:7005) in dark elec. discharge (254); from ethyl chloride (3:7015) with  $Cl_2$  in light (255), with  $NCl_3$  (256), or with  $SbCl_5$  in s.t. at 100° (257); from 1,2-dibromoethane (ethylene dihydride) (1 mole) with  $SbCl_5$  (2 moles) (note that use of only 1 mole  $SbCl_5$  yields ethylene chlorohydride) (258); from 1-chloro-2-iodoethane (ethylene chloro-iodide) with finely divided Ag at 160° (259) see indic. refs.]

[For formn. of  $\bar{C}$  (together with other prods.) from ethylene glycol (1:6465) with excess fuming  $HCl$  in s.t. at 100° (260), with  $PCl_3 + ZnCl_2$  (57% yield (261)), with  $PCl_5$  (262), or  $PCl_5 + ZnCl_2$  (37% yield (261)), with  $SOCl_2 + pyridine$  (62% yield (261)) see indic. refs.; from ethylene oxide (1:6105) with  $S_2Cl_2$  (263); from 1,4-dioxane (1:6400) with Zn + acid chlorides (264); from 2-chloroethanol-1 (ethylene chlorohydrin) (3:5552) by disproportionation in s.t. at 184° for 10 hrs. (265) or during reactn. with  $HBr$  (266); from *bis*-( $\beta$ -chloroethyl) sulfite with  $Cl_2$  (267); from *bis*-( $\beta$ -chloroethyl) sulfate with conc. aq.  $HCl$  (268) or with alk. chloride + dil.  $HCl$  (269) see indic. refs.]

[For formn. of  $\bar{C}$  (together with other prods.) from diazomethane with  $ZnCl_2$  in ether (270), from ethylenediamine with  $NOCl$  in xylene (271), see indic. refs.]

[For prepn. of "heavy"  $\bar{C}$  contg. 1  $C^{13}$  atom (from  $NaC^{13}N$  via  $CH_3C^{13}N$ ,  $CH_3C^{13}H_2NH_2$ ,  $CH_3C^{13}H_2N(CH_3)_2OH$ ,  $CH_2=C^{13}H_2$ ) and its reactn. with  $Cl_2$  see {272}.]

### CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis of  $\bar{C}$ .  $\bar{C}$  on suitable htg. especially in pres. of dehydrohalogenating cat. loses 1 mole  $HCl$  yielding vinyl chloride (3:7010) [e.g.,  $\bar{C}$  over activated carbon at 230–250° (273), or with aq. vapor over cat. at 800–1000° (274), or over pumice at 600° (275) cf. (276) (277), or over alumina at low red heat (278) yields vinyl chloride (3:7010)].

### BEHAVIOR OF $\bar{C}$ WITH INORGANIC REACTANTS

Reaction of  $\bar{C}$  with  $Cl_2$ .  $\bar{C}$  with  $Cl_2$  gives according to the conditions chlorinated derivatives either of the ethylene or ethane series.

[E.g.,  $\bar{C}$  with  $Cl_2$  in pres. of  $AlCl_3/NaCl/FeCl_3$  at 400–480° gives (279) a mixt. contg. 20% 1,1-dichloroethylene (3:5005) + 22% 1,2-dichloroethylene (3:5036) + 29% trichloroethylene (3:5170) + 29% higher chlorination prods.;  $\bar{C}$  with  $Cl_2$  over suitable cat. at 300–500° gives (280) tetrachloroethylene (3:5460)]

[On the other hand,  $\bar{C}$  with  $Cl_2$  in ultra-violet light at 50° (281) (282), or 25° (283), or  $\bar{C}$  with  $Cl_2$  + suitable cat. at not above 60° (284), or  $\bar{C}$  (as liquid) with  $Cl_2$  (285), or  $\bar{C}$  with  $Cl_2$  in pres. of  $AlCl_3/NaCl/FeCl_3$  at 300–425° as directed (279), or  $\bar{C}$  with  $SO_2Cl_2$  + trace of dibenzoyl peroxide refluxed 2 hrs. in dark (286) gives (yields: 80% (284), 70% (283) (286), 50% (279)) 1,1,2-trichloroethane (3:5330). — Furthermore,  $\bar{C}$  with  $Cl_2$  as directed (287) (288) or  $Cl_2$  +  $AlCl_3$  at 70–80° (289) (327) gives 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). — Finally  $\bar{C}$  (in vapor phase) with  $Cl_2$  + cat. (290) cf. (285) or  $\bar{C}$  with  $Cl_2$  at elev. temp. and press. (291) yields hexachloroethane (3:4835).]

Reaction of  $\bar{C}$  with alkalis.  $\bar{C}$  with alkalis or substances behaving as such may according to circumstances undergo either (or both) of two reactions: on the one hand  $\bar{C}$  may lose  $HCl$  (1 mole) (dehydrohalogenation) yielding vinyl chloride (3:7010); on the other  $\bar{C}$  may be hydrolyzed to ethylene glycol (1:6465).

Dehydrohalogenation.  $\bar{C}$  with aq. alk. at elev. temp. and press. (292) especially in pres. of tetramethylene glycol, etc. (293), or  $\bar{C}$  with  $MeOH/alk.$  (294), or  $EtOH/alk.$  (53) (295), loses  $HCl$  giving (91–93% yield (53)) vinyl chloride (3:7010). — [For study of rate of reactn. of  $\bar{C}$  with  $KOH$  in 95%  $EtOH$  at 90° and 100° (296) (297), with  $NaOEt$  or  $KOEt$  in 95%  $EtOH$  or 48%  $EtOH$  at 90° (296) (297), or with  $MeOH/NaOMe$  at 17–19° (298) see indic. refs. — Note that  $\bar{C}$  with alc.  $NaOEt$  at 100° under press. gives 90% yield (299) ethyl vinyl ether (1:7810).]

Hydrolysis.  $\bar{C}$  under appropriate conditions hydrolyzes to ethylene glycol (1:6465); for general articles from this viewpoint see (110) (214) (314).

[For hydrolysis of  $\bar{C}$  to ethylene glycol with aq. vapor over cat. at 550–850° (300), with aq. at 200° under press. in absence of any acid acceptor (301), or with aq. at 120° under press. (302) see indic. refs. cf. (110).]

[For hydrolysis of  $\bar{C}$  to ethylene glycol with aq.  $KOH$  at elevated temp. and press. see (110). — For study of use of  $Na_2CO_3$  and/or  $NaHCO_3$  in aq. (214) (303) (304) (305) (306) or in 85%  $EtOH$  (307) cf. (214) see indic. refs. — For use of aq.  $CaCO_3$  in pres. of  $NH_4$  salts (308) (309), or aq.  $BaCO_3$  (310) at elev. temp. and press., see indic. refs. — For use of sodium formate in  $MeOH$  at 165° under press. (311) cf. (214), aq. +  $PbO$  in s.t. at 170° (312), or  $Fe_2O_3$  (?) (313) see indic. refs.]

For use of hydrolysis with alk. followed by  $KMnO_4$  oxidn. of resultant ethylene glycol to oxalic acid as means of distinction between  $\bar{C}$  and the isomeric 1,1-dichloroethane (3:5035) see (256).



[For prepn. of "heavy lactn. of  $\bar{C}$  with aq. 2,4-dichlorophenol (3:0560) or with 2,4,6-tri- $H_2NH_2$ ,  $CH_2C^{12}H_2N(C^{13})$  at 73-98° for 24-66 hrs. giving respectively 1,2-bis-(2,4-dichlorom.p. 132-133°, and 1,2-bis-(2,4,6-trichlorophenoxy)ethane, m.p. 167-

of  $\bar{C}$  with 50% NaOH + cellulose see (358). —  $\bar{C}$  with MeOH over  $Al_2O_3$  Pyrolysis of  $\bar{C}$ , HCl yielding (359) vinyl chloride (3:7010) + MeCl (3:7005).] 1 mole HCl yield. of "heavy"  $\bar{C}$ , viz.,  $ClCH_2C^{12}H_2Cl$ , with "heavy" benzyl mercaptan, (273), or with  $CH_2S^{34}H$ , see (272).]

(276) (277), on of  $\bar{C}$  with salts of organic acids.  $\bar{C}$  with salts of acids yields the corresp. ethylene sters; note, however, that reactn. of only 1 chlorine atom can lead to  $\beta$ -chloroethyl and that loss of HCl and subsequent formn. of vinyl esters (or their polymers) can

React-imes occur.

times ei- $\bar{C}$  with NaCN yields (360) succino(di)nitrile [Beil. II-615, II<sub>1</sub>-(265), II<sub>2</sub>-(554)], [E.g. 53-54° (for rate of reactn. of  $\bar{C}$  with alc. KCN see (296)). —  $\bar{C}$  with anhydrous alkali 20% alk.-earth acetate at 230° in glycol diacetate (361) or monoacetate (364), or in alc. at chlc. 0-180° under press (302), or in pres. of an amine salt as cat. at 175-225° (363), yields cat. thylene glycol diacetate (1:3511), b.p. 190°.]

(U) Reaction of  $\bar{C}$  with miscellaneous non-nitrogenous org. cpds. [For reactn. of  $\bar{C}$  +  $Cl_2$  (in  $CCl_4$ ) with CO at 60-70° and 60-70 atm. press. yielding a mixt. of acid chlorides, with  $Cl_2$  ones, etc., see (365). — For reactn. of  $\bar{C}$  with  $CS_2$  + aq. KOH yielding ethylene glycol fluocarbonate see (366)]

trace of  $\bar{C}$  (0.5 mole) + ethylene dibromide (0.5 mole) +  $AlCl_3$  (0.015 mole) refluxed 2 hrs. (283) (287) or stood at 25° for 35 hrs. (368) undergoes a redistribution reaction giving a prod. itg. 49.8 mole % 1-bromo-2-chloroethane [ethylene chlorobromide] [Beil. I-89, I<sub>1</sub>-(28), (acetyl (61)], h.p. 107-108°,  $n_D^{20} = 1.4008$  (369) — Similarly  $\bar{C}$  (1 mole) + ethyl bromide of (283) moles) +  $AlCl_3$  (3%) in steel bomb at 25° for 14 days gives a mixt. contg. five prods. React. mole % as follows.  $\bar{C}$  9%, EtCl 34%, ethylene chlorobromide 18%, ethylene dibromide cording %, and EtBr 29% (367)]

may be. For reactn. of  $\bar{C}$  with diethyl sodio-malonate leading to tetraethyl butane-1,1,4,4- other  $\bar{C}$  racarboxylate [Beil. II-862, II<sub>1</sub>-(333), II<sub>2</sub>-(702)] together with various other prods. see (283) (371).]

of tetram. reactn. of  $\bar{C}$  with amines.  $\bar{C}$  with aniline (4 moles) boiled  $\frac{3}{4}$  hr. yields (372)  $N,N'$ - loses  $HCl$  phenyl-ethylenediamine (1,2-bis-(phenylamino)ethane) [Beil. XII-543, XII<sub>1</sub>-(282)], reactn. of  $\bar{C}$  4% (373) (corresp. bis-acetyl deriv. m.p. 158°), probably accompanied by some  $N,N'$ - 95%  $N,N'$ -diethylpiperazine [Beil. XXIII-8, XXIII<sub>1</sub>-(5)], m.p. 164°. [For nitration of 1,2-bis- reactn. of  $\bar{C}$  (1 mole) +  $AlCl_3$  (3%) in steel bomb at 25° for 14 days gives a mixt. contg. five prods. React. mole % as follows.  $\bar{C}$  9%, EtCl 34%, ethylene chlorobromide 18%, ethylene dibromide cording %, and EtBr 29% (367)].

that  $\bar{C}$  with  $NaNHC_6H_5$  (from aniline +  $NaNH_2$  in dry ether) loses 2 HCl yielding (371) (371).]  $\bar{C}$  with 33% abs. alc.  $Me_3N$  stood 10 days gives (22.5% yield (376)) the corresp. mono- ternary salt,  $\beta$ -chloroethyl-trimethyl-ammonium chloride ("choline dichloride"); study of rate of reactn. of  $\bar{C}$  with  $Me_3N$  in 90% acetone at 55° see (377). — For studies to rate of reactn. of  $\bar{C}$  with other amines, e.g., with benzylamine (296) (297), piperidine (297) (298), pyridine (298) (378), see indic. refs.]

## COLOR REACTIONS OF $\bar{C}$

$\bar{C}$  (2 drops) with 2% soln. of phenolphthalein in cyclohexanol (2 ml.) + trace solid NaOH htd. 5 min. at 190-200° (preferably in bath as directed (379)), when cooled and acidified with AcOH (1 ml.) gives lilac color. [Note that acetylene tetra- chloride (3:5750) with this reagt. gives a somewhat similar result.]

Comment on  $\text{NH}_4\text{OH}/\text{CuCl}$  reagent. Note that  $\bar{\text{C}}$  with  $\text{NH}_4\text{OH}/\text{CuCl}$  does not (380) give any color (dif. from 1,1-dichloroethane (ethylidene (di)chloride) (3:5035) which in 10 min. gives cloudy amethyst coloration (380)).

Comment on Fehling's soln. Note that  $\bar{\text{C}}$  does not reduce Fehling's soln. even on htg. (dif. from ethylidene (di)chloride (3:5035)).

① 1,2-Diphenoxyethane (ethylene glycol diphenyl ether) (1:7235). Lfts. from alc., m.p. 98°. [From  $\bar{\text{C}}$  with aq. K phenolate refluxed 48 hrs. (70–85% yield (353)); note, however, that if only one of the two chlorine atoms reacts some  $\beta$ -chloroethyl phenyl ether, m.p. 28°, b.p. 217–220° at 760 mm. (355), may be formed.]

— 1,2-Di- $\alpha$ -naphthoxyethane (ethylene glycol di- $\alpha$ -naphthyl ether) [Beil. VI-607]. Lfts. from nlc., m.p. 127.5° (381). [From  $\bar{\text{C}}$  +  $\alpha$ -naphthol + aq. NaOH at 120° in s.t. for 8 hrs. (381). — Note that the half reactn. prod.,  $\beta$ -chloroethyl  $\alpha$ -naphthyl ether, has m.p. 28° (355).]

— 1,2-Di- $\beta$ -naphthoxyethane (ethylene glycol di- $\beta$ -naphthyl ether) [Beil. VI-612]. Lfts. from  $\text{C}_6\text{H}_6$ , m.p. 217° (381). [From  $\bar{\text{C}}$  +  $\beta$ -naphthol + aq. NaOH at 120° in s.t. for 8 hrs. (381). — Note that the half reactn. prod.,  $\beta$ -chloroethyl  $\beta$ -naphthyl ether, has m.p. 83° (355).]

② Ethylene 1,2-bis-(isothioureac plcrate): ndls. from alc., m.p. 260° (382), 250° (332). [From  $\bar{\text{C}}$  with thiourea refluxed in nlc. and subsequently treated with  $\text{KOH}$  (332).]

③ 1,2-Diphthalimidoethane (ethylene diphthalimide) [Beil. XXI-402, XXI-(384)]. Ndls. from  $\text{AcOH}$ , dil.  $\text{AcOH}$  or alc., m.p. 236° (383), 232–233° (384), 232° (385). [From  $\bar{\text{C}}$  + K phthalimide (2 moles) in s.t. at 200° (386); note that  $\bar{\text{C}}$  in very large excess with K phthalimide in s.t. at 180–190° for 3 hrs. gives (387) the half reactn. prod.,  $N$ -( $\beta$ -chloroethyl)phthalimide, cryst. from  $\text{CS}_2$  or alc., m.p. 81° (388), 79–81° (387) (389).]

— 1,2-Disaccharinoethane: m.p. 253–254° (392). [Not reported from  $\bar{\text{C}}$  itself, but ohtd. (20% yield) from ethylene (di)bromide with sodium saccharin in aq. butyl-carbitol (1:6517) contg. KI on refluxing for 3 hrs.; note that with shorter reflux (1 hr.) some half reactn. prod., viz.,  $N$ -( $\beta$ -bromoethyl)saccharin, m.p. 99°, is formed (392).]

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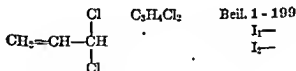
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## 3:5140 3,3-DICHLOROPROPENE-1

(1,1-Dichloropropene-2;  
allylidene (di)chloride;  
"acrolein dichloride")



B.P. 84.4° cor. (1)  
85° (5)

$D_{20}^{25} = 1.170$  (1)  
 $D_{20}^{25} = 1.169$  (2)

$n_D^{25} = 1.450$  (2)

[See also 1,3-dichloropropene-1 (3:5280).]

Note that  $\bar{C}$  represents the synionic mesomer of 1,3-dichloropropene-1 (3:5280); reactions of either mesomer may under certain conditions lead to derivatives of the other; however, in practice the tendency appears to be strongly in the direction of 1,3-dichloropropene-1 (3:5280) so that most of the known reactions of  $\bar{C}$  yield the same products as does the mesomer; the rate of reaction, however, is generally very much slower with  $\bar{C}$ .

[For prepn. of  $\bar{C}$  from acrolein (1:0115) with  $\text{PCl}_5$  (16% yield  $\bar{C}$  accompanied by 32% 1,3-dichloropropene-1 and some 1,1,3-trichloropropene (3:5660) (3)) (1) (4), or from 1,1,3-trichloropropene (3:5660) with alc.  $\text{KOH}$  (5) (other products are also formed), see indic. refs.]

[ $\bar{C}$  with  $\text{Cl}_2$  adds 1 mole halogen giving (4) 1,1,2,3-tetrachloropropane (3:6035), h.p. 179-180° at 756.6 mm. (4).]

[ $\bar{C}$  with conc. HCl in s.t. at  $100^\circ$  for 10 hrs. (4) isomerizes to 1,3-dichloropropene-1 (3:5280).]

[ $\bar{C}$  with NaOEt reacts much more slowly than its mesomer; however, after 15 hrs. refluxing with large excess NaOEt,  $\bar{C}$  gives 1-chloro-3-ethoxypropene [Beil. I-439], b.p.  $126-127^\circ$ ,  $D_4^{16} = 1.018$ ,  $n_D^{16} = 1.438$  (3), i.e., the same product as from the mesomer.]

[ $\bar{C}$  with Na phenolate in abs. alc. refluxed for 4 hrs. gives (3)  $\omega$ -chloroallyl phenyl ether, the same prod. as correspondingly obtd. in  $\frac{1}{2}$  hr. from the mesomer, q.v.]

[ $\bar{C}$  with  $Et_2NH$  in dry ether for 20 days gives (3) only a slight ppt. of diethylamine hydrochloride and but very small yield of  $N,N$ -diethyl- $\gamma$ -chloroallylamine (cf. the mesomer).]

[ $\bar{C}$  with NaOAc (3),  $CaBr_2$  (3),  $CaI_2$  (3) cf. (6), or  $C_6H_5MgBr$  (3) gives more slowly and in poor yields the same products as are formed readily from the mesomeric 1,3-dichloropropene-1 (3:5280), q.v.]

3:5140 (1) Hübner, Geuther, *Ann.* 114, 36-43 (1860). (2) Kirmann, Grard, *Compt. rend.* 190, 876-878 (1930), *Cent.* 1930, II 29; *C.A.* 24, 3750 (1930). *Bull. soc. chim.* (4) 47, 834-847 (1930). (3) Kirmann, Pacaud, Doque, *Bull. soc. chim.* (5) 1, 560-871 (1931). (4) van Romburgh, *Bull. soc. chim.* (2) 36, 549-557 (1881). (5) van Romburgh, *Bull. soc. chim.* (2) 37, 98-103 (1882). (6) van Romburgh, *Rec. trav. chim.* 1, 234-237 (1882).

3:5150 1,2-DICHLOROPROPENE-1  $CH_2=C=CH$   $C_3H_4Cl_2$  Beil. I - 199  
(high-boilg. stereoisomer)  $\begin{array}{c} Cl \\ | \\ Cl \end{array}$   $\begin{array}{c} I_1- \\ I_2- \end{array}$

B.P.  $84-86^\circ$  (1)

[See also the lower-boilg. stereoisomer (3:5110)]

[For prepn. of  $\bar{C}$  from  $\alpha,\beta,\beta$ -trichloro- $n$ -butyric acid (3:0925) by soln. in aq.  $Na_2CO_3$  and subsequent decompn. to  $\bar{C}$  (63% yield) by protracted boilg. see (1).]

$\bar{C}$  with  $Cl_2$  adds 1 mole halogen giving (1) 1,1,2,2-tetrachloropropane (3:5825), b.p.  $153-154^\circ$  (1)

3:5150 (1) Szenic, Taggesell, *Ber.* 28, 2667-2668 (1895).

3:5160  $\alpha$ -CHLOROPROPIONALDEHYDE  $\begin{array}{c} H \\ | \\ CH_3-C-CHO \\ | \\ Cl \end{array}$   $C_3H_5OCl$  Beil. I - 632  
 $\begin{array}{c} I_1-(334) \\ I_2- \end{array}$

B.P.  $86^\circ$  (1)

$D_4^{15} = 1.182$  (1)

$n_D^{17} = 1.431$  (1)

Oil, spar. sol. aq.; misc. with ether, AcOH, or  $C_6H_6$  —  $\bar{C}$  with aq. yields a hydrate, b.p.  $80.5-81^\circ$  (2).

$\bar{C}$  polymerizes in air to a white solid which upon htg. at  $170-200^\circ$  regenerates  $\bar{C}$  (2).

[For prepn. from  $n$ -propyl alc. (1:6150) by actn. of  $Cl_2$  at  $45-50^\circ$  in presence of catalysts such as  $AlCl_3$ ,  $CrO_2Cl_2$ , or Mg turnings see (3); for formn. (together with other products) from propylene oxide (1:6115) +  $S_2Cl_2$  see (4); for other modes of formn. see Beil. I-632 and I<sub>1</sub>-(334).]

$\bar{C}$  on oxidn. with excess alk.  $KMnO_4$  yields acetic acid ac. (1:1010) (1) (2). —  $\bar{C}$  reduces  $NH_4OH/AgNO_3$  in the cold and Fehling's soln. on htg. —  $\bar{C}$  gives positive fuchsin ald. test and yields a  $NaHSO_3$  cpd. (1).

3:5160 (1) Brochet, *Ann. chim.* (7) 10, 341-344 (1897). (2) Oddo, Cusmano, *Gazz. chim. ital.* 41, II 232-234 (1911). (3) Bowman, *Proc. S. Dakota Acad. Sci.* 19, 112-114 (1930); *C.A.* 34, 2786 (1910). (4) Malinowski, *J. Gen. Chem. (U.S.S.R.)* 9, 832-839 (1939); *C.A.* 34, 375 (1940).

3:5170 1,1,2-TRICHLOROETHYLENE  $\text{HC}=\text{C}-\text{Cl}$   $\text{C}_2\text{HCl}_3$  Beil. I - 187  
 $\text{Cl}$   $\text{Cl}$   $\text{I}_1-(78)$   
 $\text{I}_2-(159)$

B.P.	F.P.				
87.55° at 765 mm.	(1) [-73° (14)]	$D_4^{25} = 1.4507$	(0)	$n_D^{25} = 1.4750$	(18)
88° at 760 mm.	(2) -83° (12)	1.4542	(5)	1.47488	(10)
87.0-87.3°					
at 763 mm.	(3) -80.4° (15)	1.4540	(17)	1.47458	(19)
87.0-87.2°					
at 760 mm.	(4) -86.9° (16)	1.454	(10)	1.4744	(8)
87.15° at 760 mm.	(5) -88° (0)			1.4742	(8)
86.95° at 760 mm.	(0)				
	(7) (15)	$D_4^{20} = 1.477$	(2)	$n_D^{20} = 1.4770$	(20)
80.9°	(8)	1.4070	(0)		
80.7° at 760 mm.	(0)	1.4055	(4)		
80.00° at 768 mm.	(10)	1.4040	(12)		
80.0-87.5°					
at 760 mm.	(11)				
85.8-80.0°					
at 741.6 mm.	(12)				
85.9-80.0°	(32)				
83° at 680 mm.	(13)				
77.0° at 562 mm.	(5)				
65.0° at 385 mm.	(5)				
51.0° at 234 mm.	(5)				
45.0° at 183 mm.	(5)				
44.15° at 177 mm.	(5)				
38.20° at 139 mm.	(5)				
30.0° at 92 mm.	(5)				
25.0° at 73 mm.	(5)				

Note 2. For  $D_4^T$  over range

Note 1. For vap. press. over range 0°-80.7° see (0).

Colorless mobile liquid with sweetish odor suggesting chloroform.  
 inflammable (see below).

### MISCELLANEOUS PHYSICAL PROPERTIES

Various solubility relationships.  $\bar{C}$  is pract. insol. aq. and eas. volatile with. (2)  
 soly. of  $\bar{C}$  in aq. at 16° = 0.081 wt. % (23), at 18° = 0.025 wt. % (23), 0.18 ml.  
 ml. aq. (24). — Soly. of aq. in  $\bar{C}$  at -30° = 0.0025 wt. %, at -20° = 0.0050 wt. %  
 -8° = 0.0075 wt. %, at 0° = 0.0100 wt. %, at 6° = 0.0125 wt. %, at 10° = 0.0170 wt. %  
 at 20° = 0.0250 wt. %, at 25° = 0.0325 wt. % (9).

[For data on soly. in  $\bar{C}$  of 248 org. cpds. see (25); for solv. actn. of  $\bar{C}$  on various dyes  
 (in connection with use of  $\bar{C}$  as dry cleaning fluid) see (26) (see also below under uses of  $\bar{C}$ ).]

[For soly. of  $\text{I}_2$  in  $\bar{C}$  over range 11-25° see (27); for use of such solns. in detn. of  $\text{I}_2$  No.  
 of oils and fats see (28). — For distrib. of  $\text{I}_2$  between  $\bar{C}$  and aq. at 25° see (30) cf. (31).]

[For soly. in  $\bar{C}$  at 20° of  $\text{HCl}$  or  $\text{H}_2\text{S}$  at 1 atm. see (32).]

[For absorption of vapors of  $\bar{C}$  by kerosene see (33).]

Effect of  $\bar{C}$  on explosive range of various gases. Air satd. with  $\bar{C}$  at 14° conts. 5.7 vol.  
 (?) %  $\bar{C}$  (34).

[Vapor of  $\bar{C}$  does not form inflammable mixts. with air at ord. temp. and press.; below

25.5°  $\bar{C}$  has insufficient vap. press. to produce inflam. mixts. at total press. of 1 atm. or above even in mixts. contg. high concns. of  $O_2$ . — At high temps. vapor of  $\bar{C}$  is inflammable in air, igniting at 463°; in oxygen at 419° (18). — Limits of inflammability of mixts. of  $\bar{C}$  with  $O_2$  are 10.30–64.5 vol. %  $\bar{C}$  (35); for study of limits of inflam. of system  $\bar{C}/O_2/N_2$  see (18) (35).]

[For study of influence of vapors of  $\bar{C}$  upon explosive regions of mixts. of air with hydrogen (36) (37), with acetylene (36), with methane (38) (39) (36) (40) (41) (42), or with carbon monoxide (34) (36) (43) see indic. refs.]

Adsorption of  $\bar{C}$  by various materials. [For study of adsorption of  $\bar{C}$  on charcoal at 20° (44) and use in detn. of  $\bar{C}$  (45) see indic. refs.; on  $MnO_2$  see (46); on dehydrated  $Al(OH)_3$  gel at 10–40° and desorption at 90–150° as means of recovery of  $\bar{C}$  see (47).]

Other physical properties. [For study of evapn. rate of  $\bar{C}$  see (48); for study of thermal conductivity of  $\bar{C}$  see (11).]

(1) Hu<sup>1</sup> contg.  $\bar{C}$  (see also below under azeotropes).  $\bar{C} + MeOH$  (1:6120): 576–578 (1930), p./vapor-liq. compn.,  $D$ /compn., and  $n$ /compn. see (49). —  $\bar{C} + EtOH$  (3) Kurrmann, diag. of b.p./vapor-liq. compn.,  $D$ /compn., and  $n$ /compn. see (49). —  $\bar{C}$  (1882). (6) van h<sup>2</sup>): for data on  $D_4^{25}$ /compn. and  $n_D^{25}$ /compn. see (10).

study of distrib. of nicotine between  $\bar{C}$  and aq. at 17° see (23).

3:5150 1,2-DICHL<sup>3</sup>). for f.p./compn. diag., eutectic, f.p. –100.2°, contg. 63.6 wt. % (high-boilg. ste. chloroethane (3:5880): for  $D_4^{25}$ /compn. data see (17) cf. (50).

$\bar{C}$  (see also below under azeotropes).  $\bar{C} + MeOH$  (1:6120)

compn. and  $n$ /compn. diag. see (49b). —  $\bar{C} + EtOH$  (1:6130) diagram in wt. % at 25° and  $n_D^{25}$ /compn. diagram in wt. % see

[See also the lower-boilg. ste.

g.  $\bar{C}$ . Binary azeotropes.  $\bar{C} + H_2O$ : gives a two-phase const.-

[For prepn. of  $\bar{C}$  from  $\alpha, \beta, \gamma$  pc), b.p. 73°, contg. 65 mole %  $\bar{C}$  (8).

subsequent decompn. to  $\bar{C}$  forms a const.-boilg. mixt., b.p. 60.2° at 760 mm.,  $D_4^{20} = 1.1643$   $\bar{C}$  with  $Cl_2$  adds 1 mole (52a) = 30 mole %  $\bar{C}$  (52a) = 51 vol. %  $\bar{C}$  (53). —  $\bar{C} + EtOH$  153–154° (1).

-boilg. mixt., b.p. 70.9° at 760 mm.,  $D_4^{20} = 1.212$ , contg. 73 wt. %

3:5150 (1) Szenic, Tagg<sup>4</sup>  $\bar{C}$  (52b) cf. (53) (54). —  $\bar{C} + n$ -propyl alc. (1:6150): forms a const.-

75° at 760 mm.,  $D_4^{20} = 1.3283$ , contg. 83 wt. %  $\bar{C}$  = 69 mole %  $\bar{C}$

3:5160  $\alpha$ -CHLOR<sup>5</sup>  $\bar{C}$  (1:6135): forms a const.-boilg. mixt., b.p. 75.5° (7), aht. 74°

$D_4^{20} = 1.22$ , contg. abt. 72 wt. %  $\bar{C}$  (70 wt. %  $\bar{C}$  (7)) = 54 mole %  $\bar{C}$

butyl alc. (1:6180): gives a const.-boilg. mixt., b.p. 86.85° at 760 mm.,

wt. %  $\bar{C}$  (55) —  $\bar{C} + isobutyl$  alc. (1:6165): forms const.-boilg. mixt., b.p.

760 mm.,  $D_4^{20} = 1.396$ , contg. 91 wt. %  $\bar{C}$  = 86 mole %  $\bar{C}$  (52e). —  $\bar{C} + ter$ -butyl

B.P. 1:6140): forms const.-boilg. mixt., b.p. 75.8° (6), 75° (52f) at 760 mm.,  $D_4^{20} = 1.326$

contg. 67 wt. %  $\bar{C}$  (6) (84 wt. %  $\bar{C}$  (52f) = 74 mole %  $\bar{C}$  (52f)). —  $\bar{C} + ter$ -amyl alc.

Oil, 60): forms const.-boilg. mixt., b.p. 84.5° (6), 84° (52g),  $D_4^{20} = 1.372$  (52g), contg.

80 wt. %  $\bar{C}$  (6) (88 wt. %  $\bar{C}$  = 83 mole %  $\bar{C}$  (52g)). —  $\bar{C} + allyl$  alc. (1:6145): forms const.-

boilg. mixt., b.p. 80.95° at 760 mm.,  $D_4^{20} = 1.335$ , contg. 84 wt. %  $\bar{C}$  = 70 mole %  $\bar{C}$  (52h).

$\bar{C} + AcOH$  (1010): forms const.-boilg. mixt., b.p. 86.5° at 760 mm., contg. 96.2 wt.

%  $\bar{C}$  (6).

$\bar{C} + 1,2$ -dichloroethane (ethylene dichloride) (3:5130): forms a const.-boilg. mixt., b.p.

82.9° at 760 mm., contg. abt. 18 wt. %  $\bar{C}$  (6).

Ternary azeotropes.  $\bar{C} + EtOH$  (1:6130) +  $H_2O$ : forms a ternary heteroazeotrope,

b.p. 67.25° at 760 mm., contg. 38.4 mole %  $\bar{C}$  + 41.2 mole %  $EtOH$  + 20.4 mole %  $H_2O$

(54a): note that this azeotrope conts. 69.4 vol. %  $\bar{C}$  + 23.8 vol. %  $EtOH$  + 6.8 vol. %

$H_2O$  (53), and that upon condensation at 15° it separates into two layers, the upper having

the composition 0.8 vol. %  $\bar{C}$  + 7.2 vol. %  $EtOH$  + 5 vol. %  $H_2O$  (total upper layer = 13



vol. %), the lower having the composition 68.6 vol. %  $\bar{C}$  + 16.6 vol. % EtOH + 1.8 vol. %  $H_2O$  (total lower layer = 87%) (53). — For further discussion and data see also (8) (49).

$\bar{C}$  + *n*-propyl alc. (1:6150) +  $H_2O$ : forms a ternary heteroazeotrope, h.p. 71.55° at 760 mm., contg. 51.1 mole %  $\bar{C}$  + 16.6 mole % *n*-propyl alc. + 32.3 mole %  $H_2O$  (56b).

$\bar{C}$  + allyl alc. (1:6145) +  $H_2O$ : forms a ternary heteroazeotrope, h.p. 71.4° at 760 mm., contg. 49.2 mole %  $\bar{C}$  + 17.3 mole % allyl alc. + 33.5 mole %  $H_2O$  (56c).

### USES OF $\bar{C}$

Most of the utility of  $\bar{C}$  in industry depends upon its physical properties especially as a solvent; these applications include the dehydration of alcohols and acids, degreasing of metal, wool, and leather, dry cleaning of fabrics, extracting of oils from seeds, etc.; dewaxing of mineral lubricating oils, use as fumigant and insecticide, refrigerant, etc. [For an excellent brief survey of these uses see (57) (58); for further and more recent examples see below.]

Use in dehydration of alcohols. [For use of  $\bar{C}$  in dehydration of EtOH (or MeOH) by azeotropic distn. (Drawinol process) see (8) (49) (53) (59) (60) (61) (62); for patents on this method see (63). — For use of  $\bar{C}$  in denaturing alc. see (64).]

Use in dehydration of acids. [For use of  $\bar{C}$  in concn. of AcOH (1:1010) see patents (65) (66). — For sepn. of AcOH (1:1010) from formic acid (1:1005) by distn. of mixt. with  $\bar{C}$ , the condensate sepg. into an upper layer of an azeotropic mixt. of  $\bar{C}$  + formic acid, the lower layer being  $\bar{C}$  see (67).]

Use of  $\bar{C}$  for degreasing of metal. [For patents on use as metal degreaser of mixts. of  $\bar{C}$  + an alc. + soap (68),  $\bar{C}$  + oleic acid (69),  $\bar{C}$  + ethylene dichloride (3:5130) (70) (71), or  $\bar{C}$  (72) (73) see indic. refs. — For use of  $\bar{C}$  + rosin + boiled linseed oil in cleaning and leaving coating preparatory to etching see (74). — Because of great toxicity of  $\bar{C}$  (see below) special attention (75) must be given to ventilation of degreasers using it.]

Use of  $\bar{C}$  in dry cleaning of fabrics. Because of its solvent power supported by its low b.p. and non-inflammability  $\bar{C}$  is widely used as dry cleaner's solvent [for general articles from this viewpoint see (76) (77) (78); for patent see (79); for solv. actn. of  $\bar{C}$  on dyes see (26)].

Use of  $\bar{C}$  in extraction of fats and oils. [For use of  $\bar{C}$  as solv. for extraction see (81) (82) (83). — For use of  $\bar{C}$  for extraction of soybean oil (84) including  $n_D^{25}$  and  $D$  in g/cc. at 77°, 100°, and 122° F. (19) see indic. refs. — For study of losses of  $\bar{C}$  in extn. of fats see (85).]

[For use of  $\bar{C}$  in detn. of fats in foods (butter, margarine, etc.) see (86) (87).]

[For use of  $\bar{C}$  in detn. of aq. in fats and oils see (88); cf. use of acetylene tetrachloride (3:5750) for this purpose.]

Use of  $\bar{C}$  in dewaxing of mineral lubricating oils. [For articles including use of  $\bar{C}$  for this purpose see (89) (90); for patents see (91).]

Use of  $\bar{C}$  as fumigant, insecticide, etc. [For comparative tests of  $\bar{C}$  see (92); for patents on such use of  $\bar{C}$  (93) or mixts. contg.  $\bar{C}$  (94) see indic. refs.]

Use of  $\bar{C}$  as component of refrigerating liquids. [For use of  $\bar{C}$  with dichloroethylene (3:5030) see (95) cf. (96); for use of  $\bar{C}$  or its mixts. in low-temp. cryostats see (16).]

Miscellaneous uses of  $\bar{C}$ . [For use of  $\bar{C}$  with MeBr (97) or with  $CCl_4$  (98) as fire extinguishing compn. see indic. refs.; for use of  $\bar{C}$  as hoiler or radiator cleaner (99) or as rust-retarder (100) see indic. refs.; for use of  $\bar{C}$  as weed-killer see (101); for addition to liq. HCN to diminish inflammability see (102); in prepn. of starch see (103); in recrystn. of T.N.T. see (104); for use as solv. in ehullioscopy ( $K = 44.3$  per 100 g. solv.) see (105); to replace xylene in histological technique see (106) (107) (108).]

PHYSIOLOGICAL BEHAVIOR OF  $\bar{C}$ 

$\bar{C}$  is one of the more toxic of the group of chlorinated solvents; it is absorbable into the body not only by inhalation but also through the skin (109). — Although full detailed treatment of this aspect of  $\bar{C}$  is beyond the scope of this work, yet the following citations will be found useful as lead references for further information.

Toxicity of  $\bar{C}$ . [For important surveys of physiological properties (110), toxicity (111), comparative toxicity of  $\bar{C}$  and  $CCl_4$  (112) see indic. refs.]

[For studies of liver injury by  $\bar{C}$  (113), of anemia from  $\bar{C}$  (114), of American cases since 1932 of industrial poisoning by  $\bar{C}$  (115), or role of impurities in toxicity of  $\bar{C}$  (116), of industrial hazards of  $\bar{C}$  (117) (118) (119), of relation between toxicity and b.p. (120) see indic. refs. — For other studies of toxicity or of poisoning by  $\bar{C}$  see (121)–(130), incl.]

$\bar{C}$  as narcotic, anesthetic, analgesic, etc. [ $\bar{C}$  has very important use in treatment of trigeminal neuralgia (131) (132) (133); for toxic effects of  $\bar{C}$  after long use as antineuralgic see (134), for chem. exam. of  $\bar{C}$  for medical use see (21).]

[For use of  $\bar{C}$  as anesthetic see (135) (136) (137); for use of  $\bar{C}$  in treatment of migraine see (138); for effect on pain threshold see (139); for neural depressing effect (140) and narcotic actn. of  $\bar{C}$  (141) (142) (143) (144) see indic. refs.]

[For studies of antiseptic and disinfectant actn. of  $\bar{C}$  see (145) (146) (147) (148) (149) (150) (24).]

Miscellaneous related topics. [From dogs after inhalation anesthesia with  $\bar{C}$  from 5–8% of initial  $\bar{C}$  is excreted (151) as trichloroacetic acid (3:1150). — For study of anthelmintic actn. of  $\bar{C}$  see (152). — For actn. of  $\bar{C}$  on alc. fermentation see (153).]

DETERMINATION OF  $\bar{C}$ 

By physical methods. For detn. of  $\bar{C}$  (as vapor) by use of the R + H "Tri-Per-Analyzer" (a recording ultra-violet photometer (154)) see (155); this instrument will measure  $\bar{C}$  in concns. of 10–2000 p.p.m. and is insensitive to methyl chloride (3:7005), methylene (di)chloride (3:5020),  $CHCl_3$  (3:5050),  $CCl_4$  (3:5100), vinyl chloride (3:7010), ethylene (di)chloride (3:5130), acetylene tetrachloride (3:5750), and to many (but not all) common non-chlorinated solvents such as methyl, ethyl, and amyl alcohols, ethyl acetate, etc.; for details see (155). — For detn. of  $\bar{C}$  in air by adsorption on charcoal see (45).

By chemical methods. Those involving decomposition of  $\bar{C}$  and subsequent detn. of resultant chloride ion. One class of these methods involves pyrolytic decomposition of  $\bar{C}$  by appropriate htg. (156) (157) cf. (158) (159) cf. (127); note that  $\bar{C}$  with air at 900–1000° gives exclusively  $CO_2 + HCl$ , provided that concn. of  $\bar{C}$  is not more than 12 mg. per liter; above this amt. from 2–20% of the total carbon and chlorine are converted to  $CO + Cl_2$ , but  $COCl_2$  (3:5000) is not found up to concns. of 100 mg.  $\bar{C}$  per liter (159). — For variation of the pyrolytic method involving burning of  $\bar{C}$  (or solns. of  $\bar{C}$ ) in a lamp see (160) (161) (162) (163) (164).

A second class involves decomposition of  $\bar{C}$  by chem. means, e.g., by use of  $Na + ethanolamine$  in dioxane (165) (166), or by complete hydrolysis of  $\bar{C}$  with excess aq. 25%  $KOH$  in s.t. at 150° for 1 hr. (167).

Note that  $\bar{C}$  on oxidn. with  $CrO_3/H_2SO_4$  as directed (168) gives quant.  $CO_2$ .

Detn. of  $\bar{C}$  by conversion to mercuric trichloroethylenide  $Hg(CCl = CCl_2)_2$ .  $\bar{C}$  with aq.  $KOH$  soln. of  $Hg(CN)_2$  on shaking 24 hrs at room temp. ppts. (169)  $Hg(CCl = CCl_2)_2$  (for amplification see below under behavior of  $\bar{C}$  with inorganic reagents.). — For use of this method in detn. of  $\bar{C}$  even in pres. of methylene (di)chloride (3:5020),  $CHCl_3$  (3:5050),  $CCl_4$  (3:5100), 1,2-dichloroethylene (3:5030), or tetrachloroethylene (3:5460) see (169).

*Detn. of  $\bar{C}$  colorimetrically by use of Fujiwara reaction with pyridine + alkali.*  $\bar{C}$  with pyridine + aq. alk. gives on short warming a red coloration (similar to but recognizably different from the red-violet color obtd. with  $\text{CHCl}_3$ ) which on further warming changes to orange; for use of this color in detn. of  $\bar{C}$  in air (accuracy  $\pm 11\%$  except that at concns. of  $\bar{C}$  as low as 20 p.p.m. error may be as much as 50%) see (170) cf. (111) (127); for use in detn. of  $\bar{C}$  in animal tissue see (171); for table of sensitivity of this test under comparable conditions from  $\bar{C}$  as compared with  $\text{CHCl}_3$  (3:5050),  $\text{CCl}_4$  (3:5100), 1,1,2-trichloroethane (3:5320), 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750), and tetrachloroethylene (3:5400) see (151).

### PREPARATION OF $\bar{C}$

The principal method of preparation or manufacture of  $\bar{C}$  is from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) by elimination of 1 HCl (see below), but it is formed as a by-product from various other reactions (see below). — [For general reviews of prepn. of  $\bar{C}$  and its relationships with other "chlorinated solvents" see (31) (172).]

From 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). *By pyrolytic loss of HCl (dehydrochlorination).* [For prepn. of  $\bar{C}$  from acetylene tetrachloride in s.t. at 300° for 15 hrs. (173), over pumice at 700° (174) or 400–500° (175), over pumice + cat. at 500° (176), over pumice contg.  $\text{Cu}_3(\text{PO}_4)_2$  at 450–500° (177), over  $\text{TbO}_2$  below 300° (178), over  $\text{BaCl}_2$  at 300° (179), over bone char at 300–310° (180), over activated carbon at 200–300° (181), 260° (182), or 500° (176) see indic. refs. — Noto claim (183) that formn. of  $\bar{C}$  by dehydrochlorination of acetylene tetrachloride over charcoal at 250–300° is not effective and yield of  $\bar{C}$  diminishes with increase of temp.]

*By pyrolytic loss of HCl in pres. of an org. acceptor.* [For prepn. of  $\bar{C}$  from acetylene tetrachloride (3:5750) or pentachloroethane (3:5880) or 1,1,1,2-tetrachloroethane (3:5555) with acetylene over cat. at 250° (181) cf. (184) or with  $\text{MeOH}$  over  $\text{Al}_2\text{O}_3$  at 280° (185) see indic. refs.]

*By loss of HCl in pres. of an inorganic acceptor.* [For prepn. of  $\bar{C}$  from acetylene tetrachloride (3:5750) by htg. with aq. alk. or alk. carbonates (186) in pres. of tetrachloroethylene glycol, etc., as promoter (187), or with aq.  $\text{Ca}(\text{OH})_2$  or alk. carbonates (186) (188) (192) (193) (for test of Ger. 171,900 (186) see (190) (191)), or with alc.  $\text{KOH}$  (194) (195) cf. (173), or with alc.  $\text{NaOEt}$  (194) see indic. refs.]

[For prepn. of  $\bar{C}$  from acetylene tetrachloride (3:5750) by elimination of 1 HCl with excess  $\text{NH}_3$  gas in pres. of aq. at 60–70° (196), with conc. aq.  $\text{NH}_4\text{OH}$  at 160–170° (196) (191) (for test of Ger. 351,463 (196) see (191)), with liq.  $\text{NH}_3$  at –40° (13) (197), or by refluxing with dry pyridine (198), or by action of  $\text{C}_6\text{H}_5\text{MgBr}$  (199) see indic. refs.]

*Note on impurities in  $\bar{C}$ .* Note that tech.  $\bar{C}$  obtained from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) by elimination of HCl often contains in its high-boilg. fractions ("Tri-Nachlauf" and "Tetra-Nachlauf") other chlorinated materials such as 1,1,2,3,4,4-hexachlorohutane (3:3155), 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), solid 1,2,3,4-tetrachlorobutadiene-1,3 (3:0370), liq. 1,2,3,4-tetrachlorobutadiene-1,3 (3:6150), and hexachloroethane (3:4835), (207). — [For use of these "Nachlaufe" as insecticides and weed-killers see (268).]

From other halogenated ethanes. [For formn. of  $\bar{C}$  from 1,2-dichloroethane (ethylene dichloride) (3:5130) as by-product (29% yield) of action of  $\text{Cl}_2$  in pres. of  $\text{AlCl}_3/\text{NaCl}/\text{FeCl}_3$  at 400–480° (200), or as by-product of actn. of  $\text{Cl}_2$  in u.v. light (201), see indic. refs.]

[For formn. of  $\bar{C}$  from 1-bromo-1,1,2-trichloroethane by elimination of HBr with hot alc. Na phenolate (60% yield) see (245).]

[For formn. of  $\bar{C}$  from pentachloroethane (3:5880) with acetylene over cat. at 250° (181), or with  $\text{H}_2$  over Ni at 270° (22) (note that  $\bar{C}$  resists further hydrogenation; also

that pentachloroethane over  $\text{NiCl}_2$  without  $\text{H}_2$  yields (22) tetrachloroethylene (3:5460)), or by actn. of  $\text{MeMgI}$  (203) see indic. refs. — For formn. of  $\bar{\text{C}}$  from 1,1,2-trichloro-1,2-dihydroethane with  $\text{H}_2$  over  $\text{Ni}$  at  $300^\circ$  or without  $\text{H}_2$  over  $\text{BaCl}_2$  at  $400^\circ$  see (202).]

From miscellaneous sources.  $\bar{\text{C}}$  is formed as a by-product of actn. of acetylene with  $\text{Cl}_2$  but no citations will be given here [for formn. of  $\bar{\text{C}}$  from chloral (3:5210) with  $\text{P}_2\text{S}_5$  at  $160\text{--}170^\circ$  (204) or from di- or tri-thioparachloral in dry distn. (205), or from 2-(trichloroacryloyl)-3-sulfamidobenzoic acid by alk. hydrolytic cleavage (206), see indic. refs.].

### CHEMICAL BEHAVIOR OF $\bar{\text{C}}$

Pyrolysis of  $\bar{\text{C}}$ .  $\bar{\text{C}}$  passed over pumice at  $700^\circ$  decomposes yielding (174) methylene (di)chloride (3:5020),  $\text{CHCl}_3$  (3:5050),  $\text{CCl}_4$  (3:5100), 1,1,1,2-tetrachloroethane (3:5555), pentachloroethane (3:5880), hexachloroethane (3:4835), 1,2-dichloroethylene (3:5030), tetrachloroethylene (3:5460), pentachlorobenzene (3:2290), hexachlorobenzene (3:4939), and other prods.]

Hydrogenation.  $\bar{\text{C}}$  resists hydrogenation even with  $\text{H}_2$  over  $\text{Ni}$  at  $270^\circ$  (22). — Note, however, that  $\bar{\text{C}}$  with  $\text{HI}$  in sunlight for 2 weeks in absence of air at room temp. is partially (25% (245)) reduced to 1,1,2-trichloroethane (3:5330).]

Oxidation.  $\bar{\text{C}}$  on total oxidation with  $\text{CrO}_3/\text{H}_2\text{SO}_4$  as directed (168) gives quant.  $\text{CO}_2$ . —  $\bar{\text{C}}$  over chlorinated  $\text{CuO}$  at  $450^\circ$  gives  $\text{CO}_2 + \text{H}_2\text{O}$  accompanied (209) by some phosgene (3:5000).

$\bar{\text{C}}$  with  $\text{O}_2$  in ultra-violet light (210) (198) (211) or in pres. of cat. (e.g.,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , etc.) (212) (213) (214) yields dichloroacetyl chloride (3:5290). — Note that  $\bar{\text{C}}$  in absence of  $\text{O}_2$  is not decomposed either by direct or diffused sunlight (9).]

[For study of auto-oxidn. of  $\bar{\text{C}}$  see (215); for study of acidity developed from  $\bar{\text{C}}$  with air or oxygen over range  $-23^\circ$  to  $150^\circ$  see (9).]

$\bar{\text{C}}$  with  $\text{O}_3$  gives (215) a very unstable ozonide which decomposes into phosgene (3:5000),  $\text{CO}$ ,  $\text{HCl}$ , and oxides of chlorine.]

Stabilization. Since in the presence of  $\text{O}_2$  (air)  $\bar{\text{C}}$  has a definite tendency toward oxidation (see above), much study has been given to the problem of its stabilization by addn. of small amts. of other materials. — [For general study of the stability of  $\bar{\text{C}}$  under a wide variety of conditions see (9); for study of method of testing stability and the efficacy of various stabilizers see (216), for use of 2–3% of  $\text{EtOH}$  (1:6130) or of cyclohexane (1:8405) as stabilizers see (217).]

For stabilization of  $\bar{\text{C}}$  a wide variety of compds. have been recommended in the patent literature [e.g., for use of 0.01% or less of hydroquinone monomethyl ether (1:1435) or hydroquinone monobenzyl ether (1:1539) see (218); for use of 0.1% or less of *p*-*ter*-butylphenol (1:1510) or *p*-*ter*-amylphenol (1:1495) see (219); for use of 0.001% *n*-hexylresorcinol (1:1465) see (220); for use of oil-sol. azo dyes contg. phenolic groups see (221); for use of various phenols, amines, and aminophenols see (222) (235); for use of very small amts. alc.  $\text{NH}_3$  see (223); for use of trimethylamine (228) di-isopropylamine (224), triethylamine (225) (226), or other alkylamines (226), various nitrogenous cpds. such as dialkylated cyanamides, allylthiourea, hexamethylenetetramine, propionitrile, etc. (227), pyridine (228), caffeine (229), see indic. refs.].

[For stabilization of  $\bar{\text{C}}$  with mercaptans, e.g., *n*-butyl mercaptan (230), with amylene (231) cf. (222), with gasoline (232), with alk. oleate (233), with fatty acids or soaps (234) see indic. refs.]

Polymerization.  $\bar{\text{C}}$  under certain conditions reacts with itself forming dimeric, trimeric, and prob. polymeric products [e.g.,  $\bar{\text{C}}$  in glass, porcelain, or enameled vessels at  $180\text{--}210^\circ$  under press. (236) and in pres. of small amts. of various antioxidants (237) gives a dimer, a hexachlorobutene (b.p.  $200^\circ$  at 710 mm.) of undetermined structure, accompanied by

higher polymers and by hexachlorobenzene (3:4939);  $\bar{C}$  at elev. temp. and press. or under reflux in pres. of peroxides (such as  $Bz_2O_2$ ) gives (238) (239) mainly dimer, accompanied by some trimer and polymer;  $\bar{C}$  with  $AlCl_3$  gives on refluxing (240) a mixt. of resinous polymers suitable (especially in mixts. with trichlorobenzene) for use as electric-insulating material].

[For copolymerization of  $\bar{C}$  with various dienes (such as chloroprene (3:7080), etc.) see (241).]

**Reaction with halogens. Behavior with fluorine.** [ $\bar{C}$  with  $F_2$  at  $0^\circ$  for 10 hrs. gives (242) by addition 1,2-difluoro-1,2,2-trichloroethane, b.p.  $72.3-72.6^\circ$ ,  $D_4^{20} = 1.5555$ ,  $n_D^{20} = 1.3967$ , accompanied by other prods. such as 1-fluoro-1,2-dichloroethylene, and a hexachlorobutene (3:9050), m.p.  $9.5-11.0^\circ$ , b.p.  $125.5^\circ$  at 25 mm.,  $D_4^{20} = 1.6880$ ,  $n_D^{20} = 1.5442$ , which, however, is not 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), etc.]

**Behavior with chlorine.**  $\bar{C}$  under appropriate circumstances adds 1 mole  $Cl_2$  giving pentachloroethane (3:5880) [e.g., for study of addn. of  $Cl_2$  at  $80^\circ$ ,  $95^\circ$ , and  $115^\circ$  in light of 4360 Å see (243); note, however, that reaction may go further and that  $\bar{C}$  with  $Cl_2$  over activated charcoal at  $60-70^\circ$  either in light or in dark gives (98% yield (244)) hexachloroethane (3:4835)].

**Behavior with bromine.**  $\bar{C}$  readily adds 1 mole  $Br_2$  (245) (even when used as  $Br_2$  aq. (202)) yielding 1,2-dibromo-1,1,2-trichloroethane, b.p.  $204^\circ$  dec. at 760 mm. (245),  $125-126^\circ$  at 85 mm. (202),  $116.5^\circ$  at 50 mm. (245),  $n_D^{20} = 1.5710$  (245). [For study of rate of addn. to  $\bar{C}$  of  $Br_2$  in  $CCl_4$  see (246).]

**Behavior with iodine or thiocyanogen.**  $\bar{C}$  does not add  $I_2$  (Wijs method) or (SCN); (Kaufmann method) (167).

**Behavior with halogen hydrides. Reactn. of  $\bar{C}$  with dry HCl.**  $\bar{C}$  (1 mole) with dry HCl gas (1.57 moles) in pres. of anhyd.  $FeCl_3$  (0.003 mole) in dark 6 days at room temp in abs. of air or peroxides, or  $\bar{C}$  (1 mole) with dry HCl gas (1.62 moles) in pres. of  $AlCl_3$  (0.004 mole) in dark 3 days at  $0^\circ$  in abs. of air or peroxides gives exclusively (245) (yields: 49% and 22%, respectively) 1,1,1,2-tetrachloroethane (3:5555). [Note that  $\bar{C}$  with dry HCl in pres. of 5-10%  $AlCl_3$  at  $30-40^\circ$  gives (86-88% (247)) 1,1,1,2-tetrachloroethane (3:5555), but that  $\bar{C} + AlCl_3$  with dry HCl at  $50^\circ$  gives also (248) the *sym*-1,1,2,2-tetrachloroethane (3:5750), two pentachlorobutadienes (cf. (249)), and hexachlorobenzene (3:4939).]

**Reaction of  $\bar{C}$  with dry HBr.**  $\bar{C}$  in the pres. of an anti-oxidant does not react with HBr even after several days at  $100^\circ$  or after 30 days in sunlight (245).

However,  $\bar{C}$  in the pres. of suitable cat. adds HBr readily, but the mode of addn. differs according to conditions: e.g.,  $\bar{C} + HBr$  in pres. of small amts.  $FeCl_3$  or  $AlCl_3$  gives exclusively in yields up to 81% (245) 1-bromo-1,1,2-trichloroethane, b.p.  $152^\circ$  at 760 mm., b.p.  $54^\circ$  at 20 mm.,  $n_D^{20} = 1.5217$  (245); but  $\bar{C}$  with HBr in pres. of air and/or peroxides gives exclusively in yields up to 91% 2-bromo-1,1,2-trichloroethane, b.p.  $171^\circ$  at 760 mm., h.p.  $68.9^\circ$  at 20 mm.,  $n_D^{20} = 1.5302$ ,  $n_D^{45} = 1.5326$  (245).

**Behavior of  $\bar{C}$  with dry HI.**  $\bar{C}$  does not add HI even after 4 days at room temp. in dark and abs. of air; on exposure of the system for 2 weeks in sunlight 25% of  $\bar{C}$  was reduced to 1,1,2-trichloroethane (3:5330) (245).

**Behavior with oxygenated mineral acids. Reaction of  $\bar{C}$  with  $H_2SO_4$ .** [ $\bar{C}$  with strong  $H_2SO_4$  at elev. temp. undergoes reactns. leading ultimately (250) (189) to high yields of chloroacetic acid (3:1370). — For patents exemplifying various conditions see (251) (252) (253) (254) (255) (256). — Note also that the  $H_2SO_4$  may be replaced by arom. sulfonic acids such as benzenesulfonic acid, etc. (257).]

[ $\bar{C}$  with fuming  $H_2SO_4$  (10%  $SO_3$ ) shaken at  $88^\circ$  for  $\frac{3}{4}$  hrs. gives (258) cf. (255) (259)  $\alpha$ -chloro- $\alpha$ -sulfoacetic acid.]

Reaction of  $\bar{C}$  with  $HNO_3$ . [ $\bar{C}$  with conc.  $HNO_3$  ( $D = 1.42$ , 4 vols.) refluxed 3 hrs. gives mainly (260) cf. (258) dichlorodinitromethane [Beil. I-78, I<sub>1</sub>-(21), I<sub>2</sub>-(44)], accompanied by some trichloronitromethane (chloropicrin); for behavior of  $\bar{C}$  with  $N_2O_5$  in s.t. at 50° for 6 hrs. see (260).]

Behavior with alkali.  $\bar{C}$  in either aq. susp. or alc. soln. does not neutralize  $N/10$  aq. alk. (261) (for contrary earlier claim see (262)), but  $\bar{C}$  with excess 2  $N$  MeOH/KOH in s.t. at 100° for 30 min. uses alk. corresp. to 2 moles, i.e., apparent Sap. Eq. =  $M.W./2 = 65.8$ .

[ $\bar{C}$  with aq. alk. or alk.-earth hydroxides at 175° under press. in pres. of copper salts is claimed (263) to yield salts of glycolic acid (1.0430).]

[ $\bar{C}$  with ether passed as vapor with  $N_2$  over solid KOH + CaO at 130° loses HCl giving (84-90% yield (264)) dichloroacetylene (3:5010) in the form of its mol. cpd. (1:1) with ether, for earlier work in which  $\bar{C}$  alone over solid granular KOH at 130° gives (65% yield (265)) dichloroacetylene (266) see indic. refs.]

[ $\bar{C}$  with EtOH/NaOEt at 60-75° condenses with elimination of NaCl giving (yields: 81% (267), 70% (268)) (269) (204)  $\alpha,\beta$ -dichlorovinyl ethyl ether (3:5540). — Note that reaction of  $\bar{C}$  with alc. NaOEt has been accompanied by spontaneous explosions or ignition (270) (271) (272), presumably because of some form of either chloroacetylene (3:7000) or dichloroacetylene (3:5010) or both cf. (273).]

[For study of stability of  $\bar{C}$  toward water under various conditions see (9); note that carefully purified  $\bar{C}$  is more stable toward aq. than ord. tech. product (274).]

Behavior with metals. [For study of corrosive action of  $\bar{C}$  on soft steel, copper, brass, lead, aluminum, etc., at temps. 50-150° under various conditions see (9) (275) (276) (277) (278) (270) (280) (281). — For study of sensitivity to mechanical shock of  $\bar{C}$  with Li, Na, K, Ca, Sr, Ba see (282).]

Behavior with inorganic metal salts. With  $AlCl_3$ . [ $\bar{C}$  with  $AlCl_3$  (4-5%) on refluxing several hours (249) or  $\bar{C}$  at 225-230° under press. in pres. of Fe cpds. (284) undergoes bimolecular condensation with elimination of HCl and formn. of pentachlorobutadienes; see also comments above on reaction of  $\bar{C}$  with HCl and remarks below on reaction of  $\bar{C}$  with other org. chlorine cpds.]

With  $AlBr_3$ . [ $\bar{C}$  with  $AlBr_3$  as directed (283) undergoes halogen interchange giving 1,1,2-tribromoethylene [Beil. I-191, I<sub>1</sub>-(81), I<sub>2</sub>-(164)], b.p. 163-164°.]

With  $FeCl_3$ . [ $\bar{C}$  with anhydr.  $FeCl_3$  in s.t. at 85° yields (215) pentachloroethane (3:5880), but various side reactions result also in some hexachloroethane (3:4835) and tetrachloroethylene (3:5460).]

Behavior with other miscellaneous inorganic reactants. [ $\bar{C}$  with excess  $Cl_2O$  in  $CCl_4$  at -20° gives (285) pentachloroethane (3:5880), chlmal (3:5210), and octachlorodiethyl ether (3:0738). —  $\bar{C}$  with nitryl chloride ( $ClNO_2$ ) in s.t. at 100° for 3 hrs. gives (286) by addn. 1,1,1,2-tetrachloro-2-nitroethane, colorless nl, b.p. 76° at 18 mm (286). —  $\bar{C}$  with  $S_2Cl_2$  in s.t. at 140-150° for some hours (no reaction in open tube) gives mainly (287) pentachloroethane (3:5880).]

[For an attempt to react  $\bar{C}$  with hydrazine hydrate in pres. of solid KOH see (288).]

## BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

(See also above under  $\bar{C}$  with alkali.)

Behavior with hydrocarbons. [ $\bar{C}$  with  $C_6H_6$  in pres. of Al/Hg yields (289) both 1,1-diphenylethane [Beil. V-605, V<sub>1</sub>-(285), V<sub>2</sub>-(511)] and 1,1,2,2-tetraphenylethane [Beil. V-739, V<sub>1</sub>-(371), V<sub>2</sub>-(673)]. —  $\bar{C}$  (1 mmole) with cyclopentadiene (2 moles) at 175-185° under press. yields (309) a Diels-Alder type adduct, b.p. 158-160° at 11 mm., which with phenyl azide gives (309) a hydrotriazole, m.p. 225-226°.]

Behavior with other halogenated hydrocarbons (for reaction of  $\bar{C}$  with itself see above under polymerization).

With  $CHCl_3$  (3:5050). [ $\bar{C}$  in the pres. of  $AlCl_3$  at  $20^\circ$  adds  $CHCl_3$  to its unsatd. linkage yielding (290) (291) 1,1,1,2,3,3-hexachloropropane (3:6460); note that at higher temp., e.g.,  $50-60^\circ$ , yield is greatly diminished and several other prods. (290) are formed.]

With  $CCl_4$  (3:5100). [ $\bar{C}$  in the pres. of  $AlCl_3$  adds  $CCl_4$  to its unsatd. linkage giving at  $20-30^\circ$  for 48 hrs. (49% yield (292)) (290) (291) 1,1,1,2,3,3,3-heptachloropropane (3:6860).]

With 1,1,2-trichloroethane (3:5330). [ $\bar{C}$  in the pres. of  $AlCl_3$  adds 1,1,2-trichloroethane to its unsatd. linkage, then loses  $HCl$ , giving after 7 days at  $40^\circ$  a small yield (293) of 1,1,1,4,4-pentachlorobutene-2 (3:9054) accompanied by much resin.]

With hexachloropropene (3:6370). [ $\bar{C}$  (1 mole) with  $AlCl_3$  + hexachloropropene (1 mole) in  $CH_2Cl_2$  (3:5020) or  $CHCl_3$  (3:5050) at  $30-37^\circ$  gives (82% yield (294)) 1,1,2,3,3,3,4,5,5,5-nonachloropentene-1, colorless liq. with cedar-like odor, b.p.  $128^\circ$  at 2-3 mm.,  $86^\circ$  at 0.2 mm.,  $D_{20}^{20} = 1.812$ ,  $n_D^{20} = 1.5703$  (294);  $\bar{C}$  (2 moles) with  $AlCl_3$  + hexachloropropene (1 mole) as directed gives in 5 hrs. at  $20^\circ$  a mixt. of two dodecachloroheptenes ( $C_7H_2Cl_{12}$ ), one m.p.  $94-96^\circ$ , the other m.p.  $58-62^\circ$  (294).]

Behavior with paraformaldehyde (1:0080). [ $\bar{C}$  with paraformaldehyde in the pres. of conc.  $H_2SO_4$  at  $20-25^\circ$ , followed by treatment with aq., yields (295)  $O=(CH_2CHClCOOH)_2$ ; note, however, that  $\bar{C}$  with paraformaldehyde + conc.  $H_2SO_4$  + an alkyl hydrogen sulfate (296) or an alcohol (297) (to yield the alkyl hydrogen sulfate) gives the corresp. alkyl esters of  $\alpha$ -chloroacrylic acid (3:1445).]

Behavior with organic OH or SH cpds. [ $\bar{C}$  with alc.  $NaOEt$  (see above under behavior of  $\bar{C}$  with alkali) at  $60-75^\circ$  gives (yields: 81% (267), 70% (268)) (269) (204)  $\alpha,\beta$ -dichlorovinyl ethyl ether (3:5540).]

[ $\bar{C}$  (1 mole) with sodium salt of  $C_6H_5SH$  (1 mole) in abs. alc. refluxed 2 hrs. gives (298) both  $\alpha,\beta$ -dichlorovinyl ethyl thioether, b.p.  $77-80^\circ$  at 30 mm., and  $C_2H_5S.CH=CH(SC_2H_5)_2$ , b.p.  $135-140^\circ$  at 20 mm.]

[ $\bar{C}$  (1 mole) with sodium salt of  $C_6H_5SH$  (either 1 mole or excess) in abs. alc. refluxed 24 hrs. gives  $\alpha,\beta$ -dichlorovinyl phenyl thioether, b.p.  $145-150^\circ$  at 22 mm. (298).]

Behavior of  $\bar{C}$  with aromatic amines. With aniline.  $\bar{C}$  (1 mole) with aniline (3 moles) + aq. 15%  $NaOH$  (3 moles) refluxed for 40 hrs., and any unreacted components then removed by steam distn., gives (crude yield 64% (288)) *N*-phenylglycine-(*N,N*-diphenylamidine),  $C_6H_5NH.CH_2.C(=N.C_6H_5).NHC_6H_5$  [Beil. XII-557] (also known as "Sabanejev's base"), colorless cryst. from  $AcOEt$  or by rapid crystn. from hot alc., m.p.  $189-190^\circ$  (288). — [Note that this Sabanejev's base may be hydrolyzed in two distinct stages: e.g., on protracted refluxing with  $EtOH$  (288) it splits off 1 mole aniline leaving *N*-phenylglycine anilide =  $C_6H_5NH.CH_2.CO.NHC_6H_5$  [Beil. XII-556], cryst. from dil. alc., m.p.  $112-113^\circ$  (288); on the other hand the Sabanejev's base (or the *N*-phenylglycine anilide) on more vigorous treatment, e.g. with boiling aq.  $Ca(OH)_2$ , etc., hydrolyzes further yielding *N*-phenylglycine (*N*-phenylaminoacetic acid) [Beil. XII-468, XII-(263)], m.p.  $127-128^\circ$  (an important starting point for prepn. of indigo). — For patents on the prepn. of *N*-phenylglycine from  $\bar{C}$  by reactn. with aniline in the pres. of aq.  $Ca(OH)_2$  at  $170-180^\circ$  under press. see (299) (300).]

[The reactn. of  $\bar{C}$  with aniline + aq. alk. to form Sabanejev's base (above) is also accompanied by various side reactions, including formn. (29% yield (301)) of 1,1,2-tri-(anilino)ethylene, m.p.  $147^\circ$  dec. (301); for further details on this and other by-products see (301) (302).]

With other aromatic amines. [For analogous behavior of  $\bar{C}$  with other aromatic prim. amines in the pres. of aq. alk., e.g., with *p*-toluidine (288) (302) (303) (note that *o*-toluidine behaves abnormally while *m*-toluidine does not react (288)),  $\beta$ -naphthylamine (302) cf.

(288), *p*-anisidine (288), *p*-phenetidine (288), *p*-aminobiphenyl (288), and many others (288) see indic. refs.]

### COLOR TESTS FOR $\bar{C}$

① Color test with  $\alpha$ -naphthol (1:1500).  $\bar{C}$  with a few drops 2% alc.  $\alpha$ -naphthol + conc.  $H_2SO_4$  (2 ml.), shaken, diluted with aq. (1-2 ml.), gives red-peach color (304). [This test was devised especially for detection of  $\bar{C}$  in oils or melted fats (2-ml. samples); in olive oil  $\bar{C}$  can be detected in 1/2000, and can also be noted in presence of castor oil, grapeseed oil, raw linseed oil, lard, etc. Note, however, that test fails with oils which have been subjected to oxidn., e.g., boiled linseed oil, and its sensitivity is improved by the pres. of reducing agts., e.g., by a trace of Zn dust (304).]

② Color test with cyclopentanol (1:6412).  $\bar{C}$  (1 drop) with cyclopentanol (2 ml.) + trace solid NaOH, boiled 25 secs., cooled, acidified with AcOH or 85%  $H_2SO_4$ , stood 1 min., and shaken gives (305) green color. [Note that this same response is also shown by 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) but not by methylene dichloride (3:5020),  $CHCl_3$  (3:5050),  $CCl_4$  (3:5100), ethylene dichloride (3:5130), pentachloroethane (3:5880), *cis* (3:5012) or *trans* (3:5028)-1,2-dichloroethylene, or tetrachloroethylene (3:5460); for sensitivity for  $\bar{C}$  see (305).]

③ Color test with pyridine and aq. alk. (Fujiwara reaction). See above under detn. of  $\bar{C}$ .

Comment on behavior of  $\bar{C}$  with  $NH_4OH/CuCl$ . Note that  $\bar{C}$  with  $NH_4OH/CuCl$  does not give blue color within 5 min. (306) (diff. from pentachloroethane (3:5880) q.v.).

④ Mercury bis-(trichloroethyleneide),  $Hg(-CCl=CCl)_2$  (see also above under detn. of  $\bar{C}$ ). —  $\bar{C}$  with aq. KOH soln. of  $Hg(CN)_2$  on shaking 24 hrs. at room temp. (169), or  $\bar{C}$  with  $HgO + NaOEt + KCN$  in alc. shaken 1 hr. at 40-60° (not higher) (307) (308) cf. (273), gives (yields. 100% (169), 90% (307)) mercury bis-(trichloroethyleneide), cryst. from ether or  $CHCl_3$ , m.p. 83° (169) (273), 82-83° (242) (note that after recrysta. from alc. n.m.p. of 141° (307) has been reported). [For behavior of ordinary 1,2-dichloroethylene with aq. alk.  $Hg(CN)_2$  solns. yielding mercury bis-(chloroacetylide)  $Hg(-C\equiv CCl)_2$ , m.p. 165°, see text of that cpd. (3:5030).]

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*Dow Chem. Co.*

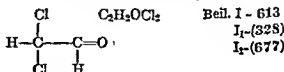
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### 3:5180 DICHLOROACETALDEHYDE



B.P. 80.5-90.5° (1)

88-90° (2) (3)

88.4-89.6° (4)

87-88° (5)

Anhydrous  $\bar{C}$  is strongly lachrymatory liq.; in a.e.  $\bar{C}$  can be kept hut in open containers it gradually changes to an amorphous polymer, insol. alc. but from which  $\bar{C}$  can be regenerated at 126° (2) cf. (6).

[For prepn. of  $\bar{C}$  from dichloroacetaldehyde diethylacetal (3:6116) hy distn. with conc.  $\text{H}_2\text{SO}_4$  (1) (2) (7) or with benzoic anhydride (1:0595) + a little conc.  $\text{H}_2\text{SO}_4$  (3) (yield: 81% (5), 78% (8)) see indic. refs.; for prepn. of  $\bar{C}$  from chloral hydrate (3:1276) with  $\text{Al/Hg}$  see (9); for manufacture of  $\bar{C}$  from chloroform + formaldehyde with  $\text{SO}_2\text{Cl}_2$  at 300° (10) or with heat, pressure, and cat. (11) see indic. refs.]

[For formn. of  $\bar{C}$  from  $\alpha,\beta,\beta$ -trichloroethyl ethyl ether (1),  $\beta,\beta$ -dichlorovinyl methyl (12) or ethyl (1) ethers on hgt. with acids; from  $\beta,\beta,\beta$ -trichlorolactic acid or its sodium salt by hgt. in  $CO_2$  (13) or warming aq. soln. (14) (22), or from its acetate with ethereal  $Et_3N$  followed by warming with aq. (13) (15); from ethyl  $\alpha$ -ethoxy- $\beta,\beta$ -dichloroacrylate on warming with aq. (16); from dichloropyruvic acid by hgt. with aq. (15) see indic. refs.]

[For formn. of  $\bar{C}$  from acetylene with  $HOCl$  (17) or from chloroacetylene (3:7000) with  $NaOCl$  (18) see indic. refs.]

$\bar{C}$  in pres. of conc.  $H_2SO_4$  polymerizes (19) to a cryst. tri (?) mer paradichloroacetaldehyde, m p. 129–130° (19), and eas. sol. alc.; this prod. on hgt. in a s.t. at 240–245° or with conc.  $H_2SO_4$  at 120–130° regenerates  $\bar{C}$ . [For use of  $\bar{C}$  and this polymer as insecticides see (20).]

$\bar{C}$  with 1 mole aq. and cooling yields (1) dichloroacetaldehyde hydrate (3:1085), m.p. 56°.

$\bar{C}$  with abs.  $EtOH$  yields (1) dichloroacetaldehyde monoethylacetal (dichloroacetaldehyde ethyl alcoholate) (3:5310). [For dichloroacetaldehyde diethylacetal, b.p. 184° see 3.6110.]

$\bar{C}$  reduces  $NH_4OH/AgNO_3$ . —  $\bar{C}$  on oxidn. with fung.  $HNO_3$  yields (21) dichloroacetic acid (3:6208).

[ $\bar{C}$  with  $PCl_5$  yields (22) 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) (which if much  $HCl$  is present may be accompanied by  $\alpha,\beta,\beta,\alpha',\beta',\beta'$ -hexachlorodiethyl ether (22)).]

$\bar{C}$  with 1 mole  $NH_2OH.HCl$  in aq. soln. yields (23) a liquid oxime, b.p. 67–69° at 17 mm., 40–44° at 2–3 mm. dec; however, with excess  $NH_2OH.HCl + Na_2CO_3$   $\bar{C}$  yields (14) (16) glyoxal dioxime (Beil I-761, I<sub>1</sub>-(394), I<sub>2</sub>-(818), m p. 177–178° (16), 173° (14).

$\bar{C}$  with excess phenylhydrazine yields (24) (25) glyoxal bis-phenylosazone, pale yel. pl. from holtg. alc., m.p. 169–171° (25), 170° (24).

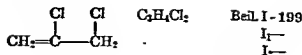
$\bar{C}$  with 1 mole semicarbazide in alc. yields (26) dichloroacetaldehyde semicarbazone, m p. 155–156° (26);  $\bar{C}$  with 2 moles semicarbazide in aq. soln. gives on boilg. (26) glyoxal bis-semicarbazone, insol. in usual solvents and not melting below 270° (27).

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(4) **5**, 414–415 (1909). (27) Harries, Temme, *Ber.* **40**, 171 (1907).



**3:5190 2,3-DICHLOROPROPENE-1**  
 ( $\beta$ -Chloroallyl chloride)


B.P. 94-94.5° (1) (6)

 $D_{25}^{25} = 1.204$  (3) $n_D^{25} = 1.4600$  (5)

94° (2) (3)

92.5° (4)

Colorless oil, insol. aq., sol. alc., ether.

[For prepn. of  $\bar{C}$  from 1,2,3-trichloropropane (3:5840) + aq. alk. (yield 80% (5), 87% (4), 70% (1)) or alc. alk. (4) see indic. refs.; for other misc. methods of formn. see Beil I-199.]

$\bar{C}$  shaken with 6-7 pts. conc.  $\text{H}_2\text{SO}_4$ , poured into aq., and distd. yields (7) chloroacetone (3:5425), b.p. 118°.

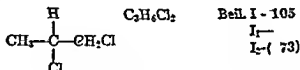
$\bar{C}$  adds  $\text{Br}_2$  giving (3) 2,3-dichloro-1,2-dibromopropane [Beil. I-112], b.p. 205° (3).

$\bar{C}$  btd. with fuming  $\text{HCl}$  in s.t. at 100° yields (3) 1,2,2-trichloropropane (3:5475), b.p. 123°.

[For study of addn. of  $\text{HF}$  see (4).]

[For use of  $\bar{C}$  in prepn. of cellulose ethers with unsatd. linkages see (8).]

3:5190 (1) Bon, *Uchenye Zapiski Leningrad. Gosudarst. Univ., Ser. Khim. Nauk.* 3, 3-37 (1935); *Cent.* 1939, II 366. (2) Kilmann, *Bull. soc. chim.* (5) 6, 546 (1939). (3) Friedel, *Silva, Jahresber.* 1871, 404; 1872, 322-323. (4) Henne, Hasekl, *J. Am. Chem. Soc.* 63, 2692-2694 (1941). (5) Hurd, Webb, *J. Am. Chem. Soc.* 59, 2191 (1936). (6) Claus, *Ann.* 170, 126 (1874). (7) Henry, *Ber.* 5, 190-191 (1872). (8) du Pont Co., *Brit.* 429,949, July 11, 1935; *Cent.* 1936, I 4093.

**3:5200 1,1,2-DICHLOROPROPANE**  
 (Propylene (di)chloride)


B.P. 96.8° at 760 mm. (1) (2)

 $D_4^{20} = 1.1545$  (6) $n_D^{20} = 1.4388$  (9)

96.4-96.6° (3) (4) (5)

96.4° at 760 mm. (6)

95.2-96.0° at 760 mm. (7) (8)

Colorless oil. — For b.p.'s at various pressures from 33-847 mm. see (6) (10). — Almost insol. in aq.; for precise data see (3) (4) (5). — [For use as technical solvent see (11); for use in concn. of  $\text{AcOH}$  by formn. with aq. of const.-boilg. mixt., b.p. 96° see (12).]

[For prepn. of  $\bar{C}$  from corresp. alc., propanediol-1,2 (propylene glycol) (1:6455), with  $\text{PCl}_3 + \text{ZnCl}_2$  (13% yield (13)), or  $\text{PCl}_3 + \text{ZnCl}_2$  (11% yield (13)), or  $\text{SOCl}_2$  (15% yield (13)), or  $\text{SOCl}_2 + \text{pyridine}$  (28% yield (13)), see (13); for prepn. of  $\bar{C}$  from propylene by addn. of  $\text{Cl}_2$  (88% yield (9)) see (9) (14) (30); for formn. of  $\bar{C}$  (35.6% (15)) together with other products by chlorination of propane (15) (16) (17) see indic. refs.; for formn. of  $\bar{C}$  (60% (18)) together with 1,3-dichloropropane (3:5450) (40% (18)) from 1-chloropropane (3:7040) with  $\text{SO}_2\text{Cl}_2$  see (18); for other misc. methods see Beil. I-105.]

[For study of limits of inflammability (3.4%-14.5% by volume) of  $\bar{C}$  in air see (19); for study of thermal conductivity of  $\bar{C}$  see (20); for adsorption of  $\bar{C}$  by activated carbon at various temps. see (31).]

$\bar{C}$  on further chlorination with  $\text{SO}_2\text{Cl}_2$  yields (18) cf. (32) 48% 1,2,2-trichloropropane (3:5475), 37% 1,2,3-trichloropropane (3:5840) cf. (21), and 15% 1,1,2-trichloropropane (3:5630).

$\bar{C}$  on htg. at 540–750°C. loses HCl yielding (15) (22) a mixt. of 3-chloropropene-1 (allyl chloride) (3:7035) and 1-chloropropene-1 (3:7030). —  $\bar{C}$  with aq. alk. under pressure and above b.p. of  $\bar{C}$  yields (23) 2-chloropropene-1 (isopropenyl chloride) (3:7020). —  $\bar{C}$  with alc. KOH (but not NaOH (9)) at 60–75° gives (95% yield (9)) mixt. of 2-chloropropene-1 (3:7020) and 1-chloropropene-1 (3:7030) cf. (21) (28).

[For reactn. of  $\bar{C}$  with salts of lower aliphatic acids yielding esters of *d,l*-propylene glycol (1:6455) see (24); with conc. aq.  $NH_4OH$  at 78–80° giving (92% yield (25)) propylenediamine dihydrochloride and other products (26) see indic. refs.]

$\bar{C}$  htd. with aq. + PbO in s.t. at 150° is said [Beil. I-103] to yield *d,l*-propylene glycol (1:6455), but  $\bar{C}$  htd. with 20 vols. aq. in s.t. at 210–220° yields (2) from the glycol a mixt. of propionaldehyde (1:0110) and acetone (1:5400). — [For behavior of  $\bar{C}$  with boilg. aq. + trace of  $NaHCO_3$ , or with boilg. aq. + Fe, see (15).]

— 1,2-Diphenoxypropane: m.p. 32°, b.p. 175–178° at 12 mm. (27). [From 1-bromo-2-phenoxypropane with 25% alc.  $NaOC_6H_5$  (27); it has not, however, been reported direct from  $\bar{C}$ .]

— 1,2-Di( $\alpha$ -naphthoxy)propane: unrecorded.

— 1,2-Di( $\beta$ -naphthoxy)propane: m.p. 152° (29). [From  $\bar{C}$  with  $\beta$ -naphthol (1:1540) + aq. NaOH in s.t. at 120° (29).]

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(21) Klebanskii, Vol'kenshtein, *J. Applied Chem. (U.S.S.R.)* 8, 106–116 (1935); *Cent.* 1935, II 3298. (22) Essex, Ward, U.S. 1,477,047, Dec. 11, 1923; *C.A.* 18, 537 (1924). (23) Young (to Carbide and Carbon Chem. Corp.), U.S. 1,752,049, March 25, 1930; *Cent.* 1930, II 1280. (24) Coleman, Moore (to Dow Chem. Co.), U.S. 2,021,852, Nov. 19, 1935; *Cent.* 1936, I 1505. (25) Darzens, *Compt. rend.* 203, 1503–1504 (1939), *C.A.* 33, 6243 (1939). (26) Mnookin, U.S. 2,049,467, August 4, 1936, *Cent.* 1937, I 1792. (27) Gilta, *Bull. soc. chim. Belg.* 31, 249 (1922). (28) Reboul, *Ann. chim.* (5) 14, 462–464 (1878). (29) Dahlen, Black, Foohey (to du Pont Co.), U.S. 1,979,141, Oct. 30, 1934; *Cent.* 1935 I 3051; [*C.A.* 29, 177 (1935)]. (30) Gavatt, *Ber.* 76, 1115–1118 (1943).

(31) Pearce, Eversole, *J. Phys. Chem.* 38, 383–393 (1934). (32) Zellner (to Tide Water Associated Oil Co.), U.S. 2,370,342, Feb. 27, 1945, *C.A.* 39 3534 (1945).

3:5210 TRICHLOROACETALDEHYDE  $\text{Cl}_3\text{C.CHO}$   $\text{C}_2\text{HOCl}_3$  Bell. I- 616  
(Chloral) Ir-(328)  
Ir-(677)

B.P.	F.P.			
97.8-98.1°	(1)	-57.5° (9)	$D_4^{25} = 1.5060$ (1) cf. (19)	
97.75° at 760 mm.	(2)		1.5049 (15) (19)	
97.73° at 760 mm.	(3)		1.5030 (9) cf. (19)	
97.7°	(4)		1.4730 (5)	
97.4-97.6° at 768 mm.	(5) (19)		$D_4^{21.4} = 1.5059$ (16)	$n_D^{21.4} = 1.45412$ (16)
97.2° cor. at 760 mm.	(6)			
			$D_4^{20} = 1.5121$ (10)	$n_D^{20} = 1.4568$ (17)
97.2° at 731.3 mm.	(7)		1.508 (16)	1.4659 (14)
97° at 747 mm.	(8)		1.5066 (14)	1.45572 (10)
97° at 740 mm.	(9)		See also Note 2.	
96-97° at 760 mm.	(10)			$n_D^{20} = 1.4548$ (16)
96.5-96.9°	(11)			
96.5°	(12) (13)		Note 1. For vapor press. of $\bar{\text{C}}$ between 0° and 30° see (18).	
96.4° at 749 mm.	(14)		Note 2. For $D_4^1$ over range 25-85° see (15).	
See also Note 1.				

[See also chloral hydrate (3:1270) and chloral ethylalcoholate (3:0860).]

Important note: The chemistry of anhydrous chloral on one hand and that of chloral hydrate on the other is so closely interwoven that the division of material between them in this book is necessarily arbitrary. For instance, there are many reactions actually employing chloral hydrate as the starting point, which by virtue of the simultaneous use of conc.  $\text{H}_2\text{SO}_4$  are undoubtedly in effect reactions of anhydrous chloral. In such cases the allocation of text between the two entries has been influenced by the nature and magnitude of the context. Although cross references have been liberally employed, the texts of both anhydrous chloral and of chloral hydrate should be compared.

### MISCELLANEOUS PHYSICAL PROPERTIES

Binary systems contg.  $\bar{\text{C}}$ .  $\bar{\text{C}}$  with  $\text{H}_2\text{O}$  combines to give chloral hydrate (3:1270) q.v. (for use in this reaction of  $\bar{\text{C}}$  in effecting drying of halogen compounds used in fire extinguishers see (20)); for extensive study of system  $\bar{\text{C}}$  + nq. see (9).

$\bar{\text{C}}$  with  $\text{EtOH}$  (1:6130) combines to give chloral ethylalcoholate (3:0860) q.v.—For analogous reactions of  $\bar{\text{C}}$  with other alcs. see below under chemical behavior of  $\bar{\text{C}}$ .

Azeotropic mixtures containing  $\bar{\text{C}}$ . A few such systems are known including the following:  $\bar{\text{C}}$  with methylcyclohexane (hexahydrotoluene) (1:8410) gives a const.-boilg. mixt., b.p. 94.45° at 760 mm., contg. 57%  $\bar{\text{C}}$  (2);  $\bar{\text{C}}$  with isobutyl formate (1:3065) gives a const.-boilg. mixt., b.p. 100.1° at 760 mm., contg. 60%  $\bar{\text{C}}$  (21);  $\bar{\text{C}}$  with *n*-propyl acetate (1:3075) gives a const.-boilg. mixt., b.p. 102.55° at 760 mm., contg. 50.5%  $\bar{\text{C}}$  (21);  $\bar{\text{C}}$  with nitromethane gives a const.-boilg. mixt., h.p. 93° at 760 mm., contg. 65%  $\bar{\text{C}}$  (20).

### PREPARATION OF $\bar{\text{C}}$

#### FROM HALOGEN-FREE STARTING POINTS

From ethyl alcohol. [ $\bar{\text{C}}$  was first prepared (22) from  $\text{EtOH}$  (1:6130) by action of  $\text{Cl}_2$ ; for discussion of mechanism of reaction see (23) (24); note that various by-products (25) (26) such as 1,1-dichloroethane (3:5035), 1,2-dichloroethane (3:5130), 1,1,2-trichloroethane (3:5330),  $\beta,\beta,\beta$ -trichloroethanol (3:5775), ethyl dichloroacetate (3:5350), and chloroform

(3:5050) have been detected; for patents on prepn. of  $\bar{C}$  (or its hydrate) from EtOH with  $Cl_2$  see (27) (28); for use of  $Cl_2$  in pres. of  $FeCl_3$  see (29).]

From acetaldehyde. [For prepn. of  $\bar{C}$  from acetaldehyde (1:0100) with  $Cl_2$  see (30) (31)]

From other non-halogenated materials. [For formation of  $\bar{C}$  from ethyl formate (1:3000) with  $SO_2Cl_2$  in s.t. at  $170^\circ$  (32) or from starch nr sucrose by distn. with  $MnO_2 + HCl$  (33) see indic. refs.]

#### FROM HALOGENATED STARTING MATERIALS

From chloro-unsaturates. [For formn. of  $\bar{C}$  from 1,1,2-trichloroethylene (3:5170) with large excess  $Cl_2O$  in  $CCl_4$  at  $-20^\circ$  (34) or on oxidn. in pres. of  $FeCl_3$ ,  $AlCl_3$ ,  $TiCl_4$ , or  $SbCl_3$  as directed (35) see indic. refs.; from chloroacetylene (3:7000) with aq. 30%  $NaOCl + H_3BO_3$  see (36).]

From carbon tetrachloride. [For prepn. of  $\bar{C}$  from  $CCl_4$  (3:5100) with formaldehyde  $+ SO_2Cl_2 + cat.$  at high temp. ( $200-500^\circ$ ) and high press. (20-200 atm.) see (401)]

From various chloral derivatives. [For prepn. of  $\bar{C}$  from chloral hydrate (3:1270) by dehydration with conc.  $H_2SO_4$  (note that  $\bar{C}$  is appreciably soluble in conc.  $H_2SO_4$  (9)) or with  $CaC_2$  slowly in cold but rapidly at  $100^\circ$  (37); from chloral ethylalcoholate (3:0860) (or other chloral alcoholates) with conc.  $H_2SO_4$ , from chloral polymers such as "metachloral" by htg. at  $180-200^\circ$  (38); from trichloroacetaldehyde diethylacetal ("trichloroacetal") (3:6317) above  $200^\circ$  (39) or on distn. with conc.  $H_2SO_4$  (39) (40); from dichloroacetaldehyde diethylacetal ("dichloroacetal") (3:6110) with  $Cl_2$  at  $60-70^\circ$  (41) see indic. refs.]

### CHEMICAL BEHAVIOR OF $\bar{C}$ WITH INORGANIC REACTANTS

#### GENERAL

[For review of chemistry of  $\bar{C}$  and its hydrate (3:1270) see (42).]

#### REDUCTION OF $\bar{C}$

According to the nature of the reagent and the conditions,  $\bar{C}$  (or its hydrate) may undergo reduction either at its  $-CCl_3$  group or at its  $-CHO$  group.

Reduction at  $-CCl_3$  group [ $\bar{C}$  with  $H_2 + Pd$  in alc.  $KOH$  (43) or with  $H_2 + Ni$  + aq. alk. (44) splits off all its halogen as  $HCl$ . —  $\bar{C}$  with  $Zn + AcOH$  (45) (46), with  $Al + AcOH$  (75), with  $Zn + strong HCl$  (47) (48), with  $Zn + dil. H_2SO_4$  (49) (50), reduces to acetaldehyde (1:0100); because of easy volatility of this product the reaction may be used for the identification and detection of  $\bar{C}$  (47) (49) (50), or for detection of  $\bar{C}$  in presence of  $CHCl_3$  (3:5050) or of  $\alpha,\alpha,\beta$ -trichloro-*n*-butyraldehyde ("butyrychloral") (3:5910) (49). — Note that  $\bar{C}$  with aq.  $Zn$  or  $Fe$  powder especially on warming gives (51)  $CH_4 + MeCl$  (3:7005)  $+ CH_2Cl_2$  (3:5020).]

[ $\bar{C}$  in aq. with  $Al/Hg$  gives (52) dichloroacetaldehyde hydrate (3:1085), while  $C$  (as hydrate) on electrolytic reduction (53) gives dichloroacetaldehyde (3:5180)  $+ chloroacetaldehyde$  (3:7212)  $+ acetaldehyde$  (1:0100)]

Reduction at  $-CHO$  group. [ $\bar{C}$  with  $Al(OEt)_3$  in abs. EtOH gives (yields: 85% (54), 84% (55), 80% (56)) (57) (58) (59) cf. (60) 2,2,2-trichloroethanol-1 (3:5775); for reduction of  $\bar{C}$  to this same product using  $Al$  isopropylate in isopropyl alc. (61) in pres. of acetaldehyde (yield 72-87% (62)),  $C_2H_5OMgBr$  (63),  $(CH_3)_2CHOMgBr$  (63), or other metallic isopropylates (64),  $ZnEt_2$  (65) (66),  $AlEt_3$  compd. with ether (88.5% yield (67)) (note, however, that  $SnEt_4$  is not effective (67)), or fermenting yeast (68) (69), see indic. refs. — For formn. of 2,2,2-trichloroethanol-1 (3:5775) during reaction of  $\bar{C}$  with various  $RMgX$  compounds see below under behavior of  $\bar{C}$  with  $RMgX$  cpds.]

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(Chloral) I- (328)  
I- (677)

B.P.	F.P.	
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97.75° at 760 mm.	(2)	1.5049 (15) (19)
97.73° at 760 mm.	(3)	1.5030 (9) cf. (19)
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96.5°	(12) (13)	Note 1. For vapor press. of $\bar{\text{C}}$ between 0°
96.4° at 749 mm.	(14)	and 30° see (18).
See also Note 1.		Note 2. For $D_4^i$ over range 25-85° see (15).

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### CHEMICAL BEHAVIOR OF $\bar{C}$ WITH INORGANIC REACTANTS

#### GENERAL

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[ $\bar{C}$  in aq. with  $Al/Hg$  gives (52) dichloroacetaldehyde hydrate (3:1085), while  $C$  (as hydrate) on electrolytic reduction (53) gives dichloroacetaldehyde (3:5180) + chloroacetaldehyde (3:7212) + acetaldehyde (1:0100).]

Reduction at  $-CHO$  group. [ $\bar{C}$  with  $Al(OEt)_3$  in abs. EtOH gives (yields: 85% (54), 84% (55), 80% (56)) (57) (58) (59) cf. (60) 2,2,2-trichloroethanol-1 (3:5775); for reduction of  $\bar{C}$  to this same product using  $Al$  isopropylate in isopropyl alc. (61) in pres. of acetaldehyde (yield 72-87% (62)),  $C_2H_5OMgBr$  (63),  $(CH_3)_2CHOMgBr$  (63), or other metallic isopropylates (64),  $ZnEt_2$  (65) (66),  $AlEt_3$  compd. with ether (88.5% yield (67)) (note, however, that  $SnEt_4$  is not effective (67)), or fermenting yeast (68) (69), see indic. refs. — For formn. of 2,2,2-trichloroethanol-1 (3:5775) during reaction of  $\bar{C}$  with various  $RMgX$  compounds see below under behavior of  $\bar{C}$  with  $RMgX$  cpds.]

OXIDATION OF  $\bar{C}$ 

$\bar{C}$  or its hydrate (3:1270) on oxidation under appropriate conditions gives trichloroacetic acid (3:1150); under some circumstances extensive decompn. also occurs (see below).

[ $\bar{C}$  on oxidn. with fumg.  $HNO_3$  (70) cf. (71), with  $HNO_2$  (72), with  $NO_2$  at 40–60° (70% yield (73)) or with aq. chlorates + cat. (74) gives trichloroacetic acid (3:1150); for formn. of latter as by-product of action of  $\bar{C}$  with  $O_2$  including comments on inhibitors, etc., see (38) (75).]

[Chloral hydrate (3:1270) on oxidn. with fumg.  $HNO_3$  (63% yield (76)) cf. (72), with  $KMnO_4$  (77) (80), with  $KClO_3$  (78), with aq. chlorates + cat. (74), or with  $Ca(OCl)_2$  (79) gives trichloroacetic acid (3:1150).]

Chloral hydrate (3:1270) reduces  $NH_4OH/AgNO_3$  (81) or Fehling's soln. (for study of sensitivity of this reaction see (82) [for oxidn. of chloral hydrate by  $HgO$ ,  $KMnO_4$ , or  $CrO_3$  see (83)]; for reduction by chloral hydrate of  $AgCl$ ,  $AgBr$ ,  $AgI$ , or  $AgSCN$  to metallic silver (84) or of alkaline solns. of Au, Ag, Bi, and Cu salts (85) see indic. refs.].

[ $\bar{C}$  in dry  $C_6H_6$  is but slowly attacked by silver oxide (86).]

REACTIONS INVOLVING DECOMPOSITION OF  $\bar{C}$ 

(See also below under behavior of  $\bar{C}$  with alkalis.)

[ $\bar{C}$  with aq.  $HIO_3$  at 100° decomposes yielding (87)  $CHCl_3$  (3:5050) +  $CO_2$  +  $ICl_3$  +  $I_2$ . —  $\bar{C}$  on chlorine-sensitized (88) or bromine-sensitized (12) photochemical oxidn. with  $O_2$  at 70–90° decomposes yielding (88) (12)  $COCl_2$  (3:5000) +  $CO$  +  $HCl$ ]

[ $\bar{C}$  on thermal decompn. at about 440°C. especially if catalyzed by  $I_2$  (89) or  $NO$  (89) (90) gives  $CHCl_3$  (3:5050) +  $CO$ .]

[ $\bar{C}$  with  $AlCl_3$  on htg. gives various products according to conditions; these include tetrachloroethylene (3:5460) (91) (92), pentachloroethane (3:5880) (93),  $\alpha,\alpha,\beta,\beta,\gamma,\gamma,\gamma$ -heptachloro-*n*-butyraldehyde ("perchlorobutanal") (94), chloral polymers (especially metachloral (91) (92) (95)), chloralide (3:3510) (92) (94), and others.]

BEHAVIOR OF  $\bar{C}$  WITH HALOGENS

With chlorine. [ $\bar{C}$  with  $Cl_2$  in sunlight decomposes giving (96)  $CCl_4$  (3:5100) +  $COCl_2$  (3:5000) +  $HCl$ ; for extensive study of photochem. reaction of  $\bar{C}$  with  $Cl_2$  at 70–90° giving  $CCl_4$  (3:5100) +  $CO$  +  $HCl$  see (97). — Note that  $\bar{C}$  with  $Cl_2$ ,  $Br_2$ , or  $I_2$  in pres. of  $AlCl_3$  gives (98) hexachloroethane (3:4835).]

With bromine. [ $\bar{C}$  with  $Br_2$  at 150° gives (99) trichloroacetyl bromide + bromotrichloromethane +  $CO$  +  $HBr$ ; for extensive study of photochem. reaction of  $\bar{C}$  with  $Br_2$  at 70–90° giving bromotrichloromethane,  $CHCl_3$  (3:5050),  $COBr_2$ ,  $CO$  +  $HBr$  see (13).]

BEHAVIOR OF  $\bar{C}$  WITH INORGANIC ACIDS

$\bar{C}$  with inorganic acids reacts in various ways according to circumstances; e.g., by formn. of addn. products, by decomposition, by formation of chloralide, by polymerization (see also its own heading below), or by combinations of these reactions.

With  $HCl$ . [ $\bar{C}$  with  $HCl$  gas at –15 to –75° yields (100) (113) an addn. product  $\bar{C} \cdot HCl$  commonly designated as chloral hydrochloride; this crystn. product with aq. dissociates giving  $\bar{C}$  (as hydrate) +  $HCl$ ; note that little, if any, polymerization occurs (100).]

With  $HBr$ . [ $\bar{C}$  with  $HBr$  gas at –15° yields (100) an addn. prod.;  $C \cdot HBr$ , similar in behavior to that of the preceding  $HCl$  addn. product.]

With  $HNO_3$ . [ $\bar{C}$  with  $HNO_3$  at 20° yields (101) an addition prod.,  $C \cdot HNO_3$ .]

With  $H_2SO_4$ . [ $\bar{C}$  with fumg.  $H_2SO_4$  contg. 2%  $SO_3$  gives on warming substantially 100% yields (102) of chloralide (3:3510); note, however, that  $\bar{C}$  with fumg.  $H_2SO_4$  contg.

10%  $\text{SO}_3$  gives nt  $0^\circ$  an addn. prod. of the type  $\text{C}_m(\text{SO}_3)_n(\text{H}_2\text{O})_p$  which on warming dec. giving  $\text{COCl}_2$  (3:5000) +  $\text{SO}_2\text{Cl}_2$  +  $\text{SO}_2$  +  $\text{CO}_2$  +  $\text{CO}$  +  $\text{HCl}$  (102); for other (older) refs. on conversion of  $\bar{\text{C}}$  with fuming  $\text{H}_2\text{SO}_4$  to chloralide (3:3510) see (61) (81) (103) (104); for conversion of chloral hydrate (3:1270) with fuming  $\text{H}_2\text{SO}_4$  to chloralide (3:3510) (yields 61% (105), 44–51% (106)) see indic. refs. — Note, however, that within a narrow range of strength (best about 79.8%)  $\text{H}_2\text{SO}_4$  appears to give with  $\bar{\text{C}}$  or its hydrate certain unstable addition products of type  $\text{CCl}_3\text{CH}(\text{OH})\text{SO}_2\text{OH}\cdot\text{H}_2\text{O}$  (148).]

With  $\text{ClSO}_3\text{H}$ . [ $\bar{\text{C}}$  with chlorosulfonic acid at  $50^\circ$  for several days gives (65% yield (107)) *bis*-( $\alpha,\beta,\beta,\beta$ -tetrachloroethyl) ether (3:0738); note that even at  $-50^\circ$  for 10–12 hrs. yield of this prod. may be as high as 50%; also that various other products including chloralide (3:3510) are also formed; and finally that  $\bar{\text{C}}$  with  $\text{FSO}_3\text{H}$  behaves similarly (107).]

### POLYMERIZATION OF $\bar{\text{C}}$

$\bar{\text{C}}$  is known to give at least three polymers; the oldest and most common polymer is that designated as "metachloral"; in addition two isomeric  $\alpha$ - and  $\beta$ -"parachlorals" (possibly comprising a pair of *cis-trans* stereoisomers) have also been reported (108).

Metachloral. [ $\bar{\text{C}}$  in presence of  $\text{H}_2\text{SO}_4$  below  $0^\circ$  (108) (sometimes suddenly cf. (109)), fuming  $\text{H}_2\text{SO}_4$  (18), pyridine (18), or  $\text{AlCl}_3$  as directed (18) (92) (110) gives metachloral [Beil. I-618,  $I_1$ -(329),  $I_2$ -(680)], a white amorphous polymer of unknown mol. wt. or structure. This polymer is insol. aq., alc., ether, or acids but dissolves in aq.  $\text{Na}_2\text{CO}_3$  forming chloral hydrate (3:1270), on distn. at  $180^\circ$  regenerates  $\bar{\text{C}}$ , oxidizes with  $\text{HNO}_3$  to trichloroacetic acid, with alkalis behaves like  $\bar{\text{C}}$  (see also below), and with  $\text{ClSO}_3\text{H}$  at  $50^\circ$  gives (107) *bis*-( $\alpha,\beta,\beta,\beta$ -tetrachloroethyl) ether (3:0738).]

Parachloral. [ $\bar{\text{C}}$  with a large excess conc.  $\text{H}_2\text{SO}_4$  at  $15$ – $20^\circ$ , carefully dissolved and stood 3 days at  $15$ – $20^\circ$ , gives in addn. to metachloral (above) and chloralide (3:3510) small amts. of two isomeric trimers, viz.,  $\alpha$ -parachloral, rhombs from hot alc., m.p.  $116^\circ$ , h.p.  $223^\circ$  at 760 mm., and  $\beta$ -parachloral, pr. from alc., m.p.  $152^\circ$ , h.p.  $250^\circ$ . Note that yield of parachloral is only about 1% of original  $\bar{\text{C}}$ , that both are more sol. in hot alc. than the main prod. metachloral, that neither form is convertible to the other or to metachloral, and that both on distn. at ord. press. dissociate to  $\bar{\text{C}}$ .]

Mixed polymers. [ $\bar{\text{C}}$  (1 mole) with acetaldehyde (3 moles) +  $\text{HCl}$  gas at  $0^\circ$  for 15–20 hrs. gives (78% yield (111)) 2,4-dimethyl-6-(trichloromethyl)-1,3,5-trioxane, h.p.  $97^\circ$  at 13 mm.,  $D_4^{20} = 1.3915$ ,  $n_D^{20} = 1.4708$ . Similar mixed polymers (presumably analogous to the preceding case) are similarly formed (112) from  $\bar{\text{C}}$  with trimethylacetaldehyde (1:0133),  $\bar{\text{C}}$  with propionaldehyde (1:0110), and  $\bar{\text{C}}$  with isobutyraldehyde (1:0120).]

Behavior of  $\bar{\text{C}}$  with alkalis.  $\bar{\text{C}}$  with conc. aq. alkalis (even in cold (22)), or  $\bar{\text{C}}$  on distn. with aq. alkalis or alk. earths (22) (114) (115), undergoes cleavage into  $\text{CHCl}_3$  (3:5050) + the corresp. salt of formic acid (1:1005); this cleavage is claimed to occur also even with conc.  $\text{NH}_4\text{OH}$  (114) or aq. amines (114) and may also produce some  $\text{CO}$  (114) and chloride ion. — [For extensive studies of kinetics of this cleavage see (116) (117) (118) (119) (120) (121) (122) (126).]

Note that  $\bar{\text{C}}$  is very stable toward hydrolysis by aq. (126) (even in s.t. at  $190$ – $200^\circ$  for 2 hrs. (118)) or by dilute acid (even in s.t. at  $150^\circ$  (118)); however,  $\bar{\text{C}}$  with aq. in sunlight is claimed (123) to give formaldehyde (1:0145) +  $\text{CO}_2$  +  $\text{HCl}$  (presumably by formn. and decompn. of  $\text{OCH}_2\text{C}(\text{OH})_2$ ), and  $\bar{\text{C}}$  with aq. is claimed (124) to undergo slight formn. of dichloroacetic acid (3:6208) +  $\text{HCl}$ .

$\bar{\text{C}}$  with alc.  $\text{KOH}$  gives (125)  $\text{CHCl}_3$  (3:5050) + ethyl formate (1:3000).

[Note that chloral deuterate,  $\text{CCl}_3\text{CH}(\text{OD})_2$  (from  $\bar{\text{C}}$  +  $\text{D}_2\text{O}$ ), with  $\text{NaOD}$  (17) or  $\text{Ca}(\text{OD})_2$  (127) in  $\text{D}_2\text{O}$  gives deuteriochloroform,  $\text{CDCl}_3$ , b.p.  $0.5^\circ$  higher than ord.  $\text{CHCl}_3$ .



OXIDATION OF  $\bar{C}$ 

$\bar{C}$  or its hydrate (3:1270) on oxidation under appropriate conditions gives trichloroacetic acid (3:1150); under some circumstances extensive decompn. also occurs (see below).

[ $\bar{C}$  on oxidn. with fumg.  $HNO_3$  (70) cf. (71), with  $HNO_2$  (72), with  $NO_2$  at 40–60° (70% yield (73)) or with aq. chlorates + cat. (74) gives trichloroacetic acid (3:1150); for formn. of latter as by-product of action of  $\bar{C}$  with  $O_2$  including comments on inhibitors, etc., see (38) (75).]

[Chloral hydrate (3:1270) on oxidn. with fumg.  $HNO_3$  (63% yield (76)) cf. (72), with  $KMnO_4$  (77) (80), with  $KClO_3$  (78), with aq. chlorates + cat. (74), or with  $Ca(OCl)_2$  (79) gives trichloroacetic acid (3:1150).]

Chloral hydrate (3:1270) reduces  $NH_4OH/AgNO_3$  (81) or Fehling's soln. (for study of sensitivity of this reaction see (82) [for oxidn. of chloral hydrate by  $HgO$ ,  $KMnO_4$ , or  $CrO_3$  see (83); for reduction by chloral hydrate of  $AgCl$ ,  $AgBr$ ,  $AgI$ , or  $AgSCN$  to metallic silver (84) or of alkaline solns. of  $Au$ ,  $Ag$ ,  $Bi$ , and  $Cu$  salts (85) see indic. refs.].

[ $\bar{C}$  in dry  $C_6H_6$  is but slowly attacked by silver oxide (86).]

REACTIONS INVOLVING DECOMPOSITION OF  $\bar{C}$ 

(See also below under behavior of  $\bar{C}$  with alkalis.)

[ $\bar{C}$  with aq.  $HIO_3$  at 100° decomposes yielding (87)  $CHCl_3$  (3:5050) +  $CO_2$  +  $ICl_3$  +  $I_2$ . —  $\bar{C}$  on chlorine-sensitized (88) or bromine-sensitized (12) photochemical oxidn. with  $O_2$  at 70–90° decomposes yielding (88) (12)  $COCl_2$  (3:5000) +  $CO$  +  $HCl$ .]

[ $\bar{C}$  on thermal decompn. at about 440°C. especially if catalyzed by  $I_2$  (89) or  $NO$  (89) (90) gives  $CHCl_3$  (3:5050) +  $CO$ .]

[ $\bar{C}$  with  $AlCl_3$  on htg. gives various products according to conditions; these include tetrachloroethylene (3:5460) (91) (92), pentachloroethane (3:5880) (93),  $\alpha,\alpha,\beta,\beta,\gamma,\gamma,\gamma$ -heptachloro-*n*-butyraldehyde ("perchlorobutanal") (94), chloral polymers (especially metachloral (91) (92) (95)), chloralide (3:3510) (92) (94), and others.]

BEHAVIOR OF  $\bar{C}$  WITH HALOGENS

With chlorine. [ $\bar{C}$  with  $Cl_2$  in sunlight decomposes giving (96)  $CCl_4$  (3:5100) +  $COCl_2$  (3:5000) +  $HCl$ ; for extensive study of photochem. reaction of  $\bar{C}$  with  $Cl_2$  at 70–90° giving  $CCl_4$  (3:5100) +  $CO$  +  $HCl$  see (97). — Note that  $\bar{C}$  with  $Cl_2$ ,  $Br_2$ , or  $I_2$  in pres. of  $AlCl_3$  gives (98) hexachloroethane (3:4835).]

With bromine. [ $\bar{C}$  with  $Br_2$  at 150° gives (99) trichloroacetyl bromide + bromotrichloromethane +  $CO$  +  $HBr$ ; for extensive study of photochem. reaction of  $\bar{C}$  with  $Br_2$  at 70–90° giving bromotrichloromethane,  $CHCl_3$  (3:5050),  $COBr_2$ ,  $CO$  +  $HBr$  see (13).]

BEHAVIOR OF  $\bar{C}$  WITH INORGANIC ACIDS

$\bar{C}$  with inorganic acids reacts in various ways according to circumstances; e g., by formn. of addn. products, by decomposition, by formation of chloralide, by polymerization (see also its own heading below), or by combinations of these reactions.

With  $HCl$ . [ $\bar{C}$  with  $HCl$  gas at –15 to –75° yields (100) (113) an addn. product  $\bar{C} \cdot HCl$  commonly designated as chloral hydrochloride; this crystn. product with aq. dissociates giving  $\bar{C}$  (as hydrate) +  $HCl$ ; note that little, if any, polymerization occurs (100).]

With  $HBr$ . [ $\bar{C}$  with  $HBr$  gas at –15° yields (100) an addn. prod.;  $C \cdot HBr$ , similar in behavior to that of the preceding  $HCl$  addn. product.]

With  $HNO_3$ . [ $\bar{C}$  with  $HNO_3$  at 20° yields (101) an addition prod.,  $C \cdot HNO_3$ .]

With  $H_2SO_4$ . [ $\bar{C}$  with fumg.  $H_2SO_4$  contg. 2%  $SO_3$  gives on warming substantially 100% yields (102) of chloralide (3:3510); note, however, that  $\bar{C}$  with fumg.  $H_2SO_4$  contg.

10%  $\text{SO}_3$  gives at  $0^\circ$  an addn. prod. of the type  $\text{C}_m(\text{SO}_3)_n(\text{H}_2\text{O})_p$  which on warming dec. giving  $\text{COCl}_2$  (3:5000) +  $\text{SO}_2\text{Cl}_2$  +  $\text{SO}_2$  +  $\text{CO}_2$  +  $\text{CO}$  +  $\text{HCl}$  (102); for other (older) refs. on conversion of  $\bar{\text{C}}$  with fuming  $\text{H}_2\text{SO}_4$  to chloralide (3:3510) see (61) (81) (103) (104); for conversion of chloral hydrate (3:1270) with fuming  $\text{H}_2\text{SO}_4$  to chloralide (3:3510) (yields: 61% (105), 44-51% (106)) see indie. refs. — Note, however, that within a narrow range of strength (best about 79.8%)  $\text{H}_2\text{SO}_4$  appears to give with  $\bar{\text{C}}$  or its hydrate certain unstable addition products of type  $\text{CCl}_3\text{CH}(\text{OH})\cdot\text{SO}_3\text{OH}\cdot\text{H}_2\text{O}$  (148).]

With  $\text{ClSO}_3\text{H}$ . [ $\bar{\text{C}}$  with chlorosulfonic acid at  $50^\circ$  for several days gives (65% yield (107)) *bis*-( $\alpha,\beta,\beta,\beta$ -tetrachloroethyl) ether (3:0738); note that even at  $-50^\circ$  for 10-12 hrs. yield of this prod. may be as high as 50%; also that various other products including chloralide (3:3510) are also formed; and finally that  $\bar{\text{C}}$  with  $\text{FSO}_3\text{H}$  behaves similarly (107).]

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$\bar{\text{C}}$  with alc.  $\text{KOH}$  gives (125)  $\text{CHCl}_3$  (3:5050) + ethyl formate (1:3000).

[Note that chloral deuterate,  $\text{CCl}_2\text{CH}(\text{OD})_2$  (from  $\bar{\text{C}}$  +  $\text{D}_2\text{O}$ ), with  $\text{NaOD}$  (17) or  $\text{Ca}(\text{OD})_2$  (127) in  $\text{D}_2\text{O}$  gives deuteriochloroform,  $\text{CDCl}_3$ , b.p.  $0.5^\circ$  higher than ord.  $\text{CHCl}_3$ ,

(3:5050), m.p.  $-64.69$  to  $-64.15^\circ$ ,  $D_4^{20} = 1.5004$  (higher than 1.4888 for  $\text{CHCl}_3$ ),  $n_D^{20} = 1.4450$  (same as  $\text{CHCl}_3$ ) (17).]

#### BEHAVIOR OF $\bar{\text{C}}$ WITH AMMONIA, HYDROXYLAMINE, HYDRAZINE, ETC.

With  $\text{NH}_3$ . [ $\bar{\text{C}}$  with dry  $\text{NH}_3$  gas (81) (48) in dry  $\text{CHCl}_3$  (128) (129) or chloral hydrate (3:1270) with  $\text{NH}_3$  in dry ether (129) gives a white solid, m.p.  $72-74^\circ$  (129),  $62-64^\circ$  (128), originally (81) (48) (128) regarded as chloralammonia  $\text{CCl}_3\text{CH}(\text{OH})\cdot\text{NH}_2$  but later (on discovery of double the expected mol. wt. (129) cf. (130)) thought to have structure  $\text{CCl}_3\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{CH}(\text{NH}_2)\cdot\text{CCl}_3\cdot\text{H}_2\text{O}$ . — The prod. with  $\text{KCN}$  in conc. aq.  $\text{NH}_4\text{OH}$  gives (93% yield (131)) dichloroacetamide, m.p.  $98.5-99.0^\circ$  (131).]

[Note that chloral hydrate (3:1270) with  $\text{NH}_4\text{OAc}$  at  $100^\circ$  gives (132) a prod., cryst. from alc., m.p.  $97^\circ$ , regarded as a dimeric form [Beil. XXIII-15] of chloralimide,  $\text{CCl}_3\text{—CH=NH}$ ; this dimer is also accompanied (132) cf. (133) by two stereoisomeric trimers [Beil. XXVI-9-10] of chloralimide.]

With hydroxylamine. The behavior of  $\bar{\text{C}}$  with hydroxylamine differs according to the circumstances employed.

[ $\bar{\text{C}}$  as chloral hydrate (3:1270) with large excess  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (4 moles) in a little aq. (134) or with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (1 mole) in pres. of conc. aq.  $\text{CaCl}_2$  (2 moles) at  $50-60^\circ$  (135) gives trichloroacetaldoxime, m.p.  $56^\circ$  (135),  $39-40^\circ$  (134), b.p.  $85^\circ$  at 20 mm. (135).]

[ $\bar{\text{C}}$  as chloral hydrate (3:1270) with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (3 moles) in aq.  $\text{Na}_2\text{CO}_3/\text{aq. NaOH}$  as directed (136) (137) gives (yields: 50% (137), 40% (136) (138)) the alkali-stable form of chloro-oximino-acetaldehyde oxime ("chloroamphiglyoxime") [Beil. III-605, III<sub>1</sub>- (216), III<sub>2</sub>-(303)], ndls. of monohydrate from boilg. aq., m.p.  $114^\circ$  (136) (138) cf. (137); note that this prod. in dry ether with  $\text{HCl}$  gas (136) or with fuming  $\text{HCl}$  (138) isomerizes to the acid-stable form ("chloroantiglyoxime") [Beil. III-606, III<sub>1</sub>-(216), III<sub>2</sub>-(303)], m.p.  $161^\circ$  (138),  $161^\circ$  dec. (136).]

[Note, however, that chloral hydrate (3:1270) (1 mole) with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (2 moles) powdered with dry  $\text{Na}_2\text{CO}_3$  (1 mole), allowed to stand in a desiccator some hours, then dissolved in aq. and extracted with ether gives (139) an addition product, cryst. from ether,  $\text{CHCl}_3$ , or  $\text{C}_6\text{H}_6$ , m.p.  $98^\circ$ , regarded as chloralhydroxylamine,  $\text{CCl}_3\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{OH}$ .]

[For behavior of  $\bar{\text{C}}$  with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  + aniline giving isatin see below under reaction of  $\bar{\text{C}}$  with primary aromatic amines.]

#### WITH HYDRAZINE

[ $\bar{\text{C}}$  as chloral hydrate (3:1270) with hydrazine hydrate in aq. (140), ether (141), or  $\text{AcOH}$  (142), or merely fused with hydrazine hydrochloride or sulfate (143), appears to give first the expected addition product, viz., chloralhydrazine,  $\text{CCl}_3\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{NH}_2$ , ndls. from alc., m.p.  $100^\circ$  (141),  $85^\circ$  dec. (140); note, however, that this structure is not certain and that the material readily changes to a compound  $\text{C}_4\text{H}_2\text{ON}_2\text{Cl}_6$ , m.p.  $187^\circ$  cf. (140) (141) (142) (143).]

#### BEHAVIOR OF $\bar{\text{C}}$ WITH MISCELLANEOUS INORGANIC REACTANTS

With various compounds of phosphorus. [ $\bar{\text{C}}$  with  $\text{PCl}_5$  in acetone gives a product regarded (144) cf. (145) as  $\text{CCl}_3\text{CH} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{PCl}_2$ , b.p.  $238-242^\circ$ , accompanied by tetrachloroethylene (3:5460) and pentachloroethane (3:5880).]

[ $\bar{\text{C}}$  with  $\text{PCl}_5\text{Br}_2$  is claimed (146) to give 1,1-dibromo-2,2,2-trichloroethane [Beil. I-93, I<sub>7</sub>-(65)], b.p.  $93-95^\circ$  at 14-15 mm.,  $D_4^{19.5} = 2.295$ ,  $n_D^{25.7} = 1.52991$  (146).]

[ $\bar{C}$  with  $P_2S_5$  in s.t. at 160–170° gives (147) a complicated reaction mixture from which only trichloroethylene (3:5170) has been identified.]

With various salts of inorganic acids (for KCN see further below).

With alkali bisulfites (or sulfites) [ $\bar{C}$  or its hydrate (3:1270) with aq. alk. bisulfites (81) (149) reacts readily; for discussion of products see (81) (150) (151).]

With hydrogen peroxide. [ $\bar{C}$  with  $H_2O_2$  in ether (151), or  $\bar{C}$  with  $K_2S_2O_8 + H_2SO_4$  at ord. temp., gives (152) "dichloralperoxide hydrate," viz.,  $CCl_3.CH(OH)-O.O.CH(OH)-CCl_3$ , cryst. from  $C_6H_6$  or  $CHCl_3$ , m.p. 122° dec.]

## CHEMICAL BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

### BEHAVIOR OF $\bar{C}$ WITH HYDROCARBONS

With alkanes. [ $\bar{C}$  with aliphatic hydrocarbons in presence of  $AlCl_3$  reacts violently, but no definite products have been isolated (153).]

With aromatic hydrocarbons.  $\bar{C}$  with aromatic hydrocarbons in presence of  $H_2SO_4$  or other condensing agent (note that, when  $H_2SO_4$  is present in large excess, chloral hydrate (3:1270) is frequently substituted for  $\bar{C}$ ) reacts in either or both of two modes:  $\bar{C}$  with 1 mole of hydrocarbon giving trichloromethyl-aryl-carbinols,  $\bar{C}$  with 2 moles of hydrocarbon giving 1,1,1-trichloro-2,2-diarylethanes. Although reaction of  $\bar{C}$  with hydrocarbons cannot here be summarized for all possible cases, yet the following examples will exemplify both modes of reaction

[ $\bar{C}$  with  $C_6H_6 + AlCl_3$  (154) (156) or chloral hydrate (3:1270) with  $C_6H_6 + AlCl_3$  (153) cf. (158) (162) or with  $C_6H_6 +$  conc.  $H_2SO_4$  (155) gives trichloromethyl-phenyl-carbinol [Beil. VI-476, VI-(237)], m.p. 37° (155), b.p. 145° at 15 mm. (155) (corresp. acetate, m.p. 87.5° (155); corresp. benzoate, m.p. 97.5° (155); corresp. *p*-nitrobenzoate, m.p. 109° (156)) accompanied (155) by 1,1,1-trichloro-2,2-diphenylethane (3:1420), the latter also obtainable from  $C + C_6H_6$  with conc.  $H_2SO_4$  (157) or with  $AlCl_3$  in  $CS_2$  (80% yield (162)).]

[ $\bar{C}$  with toluene +  $AlCl_3$  (154) or chloral hydrate (3:1270) (3 moles) with toluene (1 mole) + conc.  $H_2SO_4$  (155) gives trichloromethyl-*p*-tolylcarbinol [Beil. VI-503, VI-(255)], m.p. 63–64° (154), 63° (155), 61.5–62.5° (159), 58–59° (160); b.p. 155° at 13.5 mm. (155), 154–156° at 13.5 mm. (154) (corresp. acetate, m.p. 107.5° (155), 105–106° (160); corresp. benzoate, m.p. 100.5° (155), 94–95° (160)). — On the other hand  $\bar{C}$  with toluene (2 moles) in pres. of  $H_2SO_4$  (161), or  $AlCl_3$  (153) in  $CS_2$  at 0° (162) gives (80% yield (162)) 1,1,1-trichloro-2,2-bis-(*p*-tolyl)ethane [Beil. V-619, V-(292), V-(522)], m.p. 89° (161) (162) (155), also obtained as by-product of the above carbinol (155); for study of loss of HCl with alc. KOH yielding 1,1-dichloro-2,2-di-(*p*-tolyl)ethylene [Beil. V-648, V-(559)], m.p. 92° (161), 85° (162) see (161) (162) (163).]

[For generally analogous behavior of  $\bar{C}$  with other aromatic hydrocarbons such as *tert*-butylbenzene (405), *m*-xylene (153) (163), ethylbenzene (155), naphthalene (164), anthracene (164), or phenanthrene (164) in presence of condensing agents see indic. refs.]

### BEHAVIOR OF $\bar{C}$ WITH ARYL HALIDES

With chlorobenzene. [That  $\bar{C}$  with chlorobenzene (3:7903) (1 mole) + conc.  $H_2SO_4$  gives the expected trichloromethyl-*p*-chlorophenyl-carbinol, b.p. 187–188° at 26 mm. (165) (corresp. acetate, m.p. 120–121° (165); corresp. benzoate, m.p. 128–129° (165)), has never been reported, this prod. having been obtd. only by condensation of *p*-chlorobenzaldehyde (3:0765) with  $CHCl_3$  (3:5030) in pres. of KOH (23.5% yield (165)).]

However,  $\bar{C}$  or chloral hydrate with chlorobenzene (2 moles) + conc.  $H_2SO_4$  gives the

extremely important 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane ("DDT") (3:3298) whose text should be consulted for further details.

With bromobenzene. [That  $\bar{C}$  with bromobenzene (1 mole) + conc.  $H_2SO_4$  gives the expected trichloromethyl-*p*-bromophenyl-carbinol, b.p. 183–187° at 18 mm. (166) (corresp. acetate, m.p. 145–147° (166)), has never been reported, this product having been obt'd. (29% yield (166)) only by reaction of  $\bar{C}$  with *p*-Br. $C_6H_4$ .MgCl.]

[However,  $\bar{C}$  or chloral hydrate (3:1270) with bromobenzene (2 moles) + conc.  $H_2SO_4$  + fung.  $H_2SO_4$  gives (167) (168) 1,1,1-trichloro-2,2-bis-(*p*-bromophenyl)ethane, m.p. 144° (167), 139–141° (168); note that this prod. with alc. KOH loses HCl, giving (82% yield (167) (168)) 1,1-dichloro-2,2-bis-(*p*-bromophenyl)ethylene, m.p. 123.5° (167), 119–120° (168).]

With iodobenzene. [The carbinol to be expected from  $\bar{C}$  with iodobenzene (1 mole) + conc.  $H_2SO_4$  has not been reported.]

[However,  $\bar{C}$  with iodobenzene (2 moles) + conc.  $H_2SO_4$  gives (155) 1,1,1-trichloro-2,2-bis-(*p*-iodophenyl)ethane, m.p. 172° (155).]

## BEHAVIOR OF $\bar{C}$ WITH ORGANIC HYDROXY COMPOUNDS

### With Alcohols

General. Since  $\bar{C}$  is an aldehyde, it may be expected (at least with the assistance of a condensing agent such as dry HCl) to react with 1 mole of an alcohol to yield the corresponding hemiacetal,  $CCl_3.CH(OH)R$ , with 2 moles of an alcohol to give the corresponding acetal,  $CCl_3.CH(OR)_2$ , particularly since both these types of products are well known.

However, the special influence of the  $-CCl_3$  group becomes apparent in this reaction and only the first type (hemiacetals) are usually obtained by direct condensation, the latter (acetals) being obtained indirectly. Moreover, members of the first group (hemiacetals) are formed with extreme ease (even in absence of condensing agents) so that, by analogy to the combination of chloral with water to give chloral hydrate (3:1276), they are generically designated as chloral alcoholates; e.g., chloral methylalcoholate, chloral ethylalcoholate, etc. Corresponding reaction of several molecules of chloral with multi-hydroxy alcohols can also occur as illustrated below.

The formation of these chloralalcoholates is profoundly influenced by conditions (especially the solvent (169)); furthermore, they readily dissociate into their original components on heating and, therefore, on heating in other alcohols (170) (171) or orthoformate esters of other alcohols (170) suffer reactions involving redistribution of the various alkyl radicals.

With monohydric alcohols. Although reaction of  $\bar{C}$  with all possible monohydric alcohols obviously cannot be included here, the following examples will serve to exemplify the reaction.

With methyl alcohol. [ $\bar{C}$  with MeOH (1:6120) (1 mole) gives (171) (172) (173) (174), trichloroacetaldehyde monomethylacetal (chloral methylalcoholate), hygroscopic ndla., m.p. abt. 50° (172), 38° (171), b.p. 116° (173), 106° (172), 98° (174) (corresp. carbamate, m.p. 121° (175)). — Note that trichloroacetaldehyde dimethylacetal,  $CCl_3.CH(OC_2H_5)_2$ ; [Beil. I-621, I<sub>2</sub>-(681)], b.p. 183.2° cor. (176), 68–69° at 10 mm. (177), is obt'd. by indirect means; note incidentally that this acetal is isomeric with butyrylchloral hydrate (3:1905) and with chloral ethylalcoholate (3:0860).]

With ethyl alcohol. [ $\bar{C}$  with EtOH (1:6130) gives trichloroacetaldehyde monoethylacetal (chloral ethylalcoholate) (3:0860), q.v. for details. For the corresp. acetal, viz., trichloroacetaldehyde diethylacetal,  $CCl_3.CH(OC_2H_5)_2$ , b.p. 201°, see its own text as 3:6317.

With *n*-propyl alcohol.  $\bar{C}$  with *n*-PrOH (1:6150) (178) (171) (170), or with NaO-*n*-Pr (179) or chloral hydrate (3:1270) with *n*-PrOH (1:6150) (170) gives (yields: 90% (178), 77-90% (170)) trichloroacetaldehyde *n*-propylhemiacetal (chloral *n*-propylalcoholate), liquid, b.p. 119-121° at 742.4 mm. (170), 120-122° (178),  $D_4^{25.7} = 1.2996$  (170),  $n_D^{25} = 1.4622$ . (Note that the corresp. trichloroacetaldehyde di-*n*-propylacetal is unreported.)

With isopropyl alcohol.  $\bar{C}$  with iso-PrOH (1:6135) (178) (171) gives trichloroacetaldehyde isopropylhemiacetal (chloral isopropylalcoholate), m.p. 47° (178), 45° (171); b.p. 108° (178) (note that the corresp. trichloroacetaldehyde di-isopropylacetal is unreported.)

With *n*-butyl alcohol.  $\bar{C}$  with *n*-BuOH (1:6180) gives (171) (179) (170) trichloroacetaldehyde *n*-butylhemiacetal (chloral *n*-butylalcoholate) (3:9843), m.p. 49-50° (180), 49° (171) (170), b.p. 120-130° at 742 mm. (170) (note that corresp. trichloroacetaldehyde di-*n*-butylacetal is unreported.)

With isobutyl alcohol.  $\bar{C}$  with iso-BuOH (1:6165) gives (180) trichloroacetaldehyde isobutylhemiacetal (chloral isobutylalcoholate), liquid, b.p. 122° without decompn. (180); note that trichloroacetaldehyde di-isobutylacetal, b.p. 211.8° at 760 mm. (181), has been prepared indirectly.)

With *sec*-butyl alcohol.  $\bar{C}$  with butanol-2 (1:6155) gives (180) (171) trichloroacetaldehyde *sec*-butylhemiacetal (chloral *sec*-butylalcoholate), m.p. 12° (171), b.p. 120-121° (180), note that the corresp. trichloroacetaldehyde di-*sec*-butylacetal is unreported.)

With *ter*-butyl alcohol.  $\bar{C}$  with *ter*-butyl alc. (1:6140) gives (171) trichloroacetaldehyde *ter*-butylhemiacetal (chloral *ter*-butylalcoholate), m.p. 43° (171) (note that the corresp. trichloroacetaldehyde di-*ter*-butylacetal is unreported.)

With other monohydric alcohols. (For analogous formn. of hemiacetals from  $\bar{C}$  with isooamyl alc. (1:6200) (180), with *ter*-AmOH (1:6160) (171), with allyl alc. (1:6145) (99), with *n*-octyl alc. (1:6235) (171), with benzyl alc. (1:6180) (171), with cinnamyl alc. (1:5920) (171), with methyl-neopentyl-carbinol (182), or with  $\beta,\beta,\beta$ -trichloro-*ter*-butyl alcohol ("Chloreton") (3:2662) (183) see indic. refs.)

With dihydric alcohols. With ethylene glycol.  $\bar{C}$  (1 mole) with ethylene glycol (1:6165) (1 mole) nt 0° for 2 weeks gives (181) cf. (185) trichloroacetaldehyde ( $\beta$ -hydroxyethyl)-hemiacetal ("chloral ethyleneglycolate"), m.p. 50-51° (181), 42° (185); note that this product with conc.  $H_2SO_4$  on stdg. or htg. loses 1  $H_2O$  with ring closure to the cyclic acetal, 2-(trichloromethyl)-1,3-dioxolane, m.p. 40° (181). — However,  $\bar{C}$  (2 moles) with ethylene glycol (1:6165) (1 mole) gives (186) cf. (185) ethylene glycol 1,2-bis-( $\beta,\beta,\beta$ -trichloro- $\alpha$ -hydroxyethyl) ether, which on distn. at ord. press. also gives (186) the above 2-(trichloromethyl)-1,3-dioxolane, m.p. 42° (186).]

With polyhydric alcohols. With glycerol. (For behavior of  $\bar{C}$  with glycerol (1:6510) see (186) (181).]

With erythritol. (For behavior of  $\bar{C}$  with erythritol (1:5825) see (186).]

With various carbohydrates.  $\bar{C}$  combines with various polyhydroxy compounds of the carbohydrate type to give products collectively designated as chloraloses. Such combinations can be effected with pentoses or hexoses, with various stereoisomers within any such group, and more than one molecule of chloral per mole of carbohydrate is sometimes involved. In the light of modern work these chloraloses are probably cyclic acetals. Although space cannot here be taken for an extensive record, the following comments will serve as starting points for further exploration.

The most important chloralose is that derived from d-glucose and often indexed as glucochloralose. Two forms of this compound are known, viz.,  $\alpha$ -glucochloralose and  $\beta$ -glucochloralose; for important studies of their structures see (187) (188). For study of  $\alpha$ -xylochloralose see (189).

For important (but older) factual data on chloraloses see (190) (191) (192).

## BEHAVIOR WITH ORGANIC ACIDS

*With Acids Containing No Other Functional Group*

[For behavior of  $\bar{C}$  with AcOH in pres. of  $AlCl_3$  see (153); with  $Hg(OAc)_2$  + ethylene in alc. soln. giving a prod. possibly having the structure  $CCl_3.CH(OC_2H_5)(OCH_2CH_2HgOAc)$  see (215).]

[Note that  $\bar{C}$  is able to add to its carbonyl group a reactive H atom derived from certain acids [e.g.,  $\bar{C}$  with malonic acid (1:0480) in AcOH at  $100^\circ$  for 40 hrs. (216) cf. (217), or in pyridine at  $100^\circ$  for 2 hrs. (67.5% yield (218)) cf. (219), or chloral hydrate (3:1270) + malonic acid (1:0480) + pyridine at  $100^\circ$  (220) gives (note loss of  $CO_2$ )  $\gamma,\gamma,\gamma$ -trichloro- $\beta$ -hydroxy-*n*-butyric acid [Beil. III-310, III<sub>1</sub>-(117), III<sub>2</sub>-(221)], m.p.  $118-119^\circ$  (217) (218),  $118.5^\circ$  (216) (note hydrate, m.p.  $52-54^\circ$  (218)); note also that by further elimination of  $H_2O$  (e.g., with  $Ac_2O$  +  $NaOAc$  (217)) this prod. yields  $\gamma,\gamma,\gamma$ -trichlorocrotonic acid [Beil. II-418, II<sub>1</sub>-(190), II<sub>2</sub>-(397)], m.p.  $113-114^\circ$  (217).]

[Similarly,  $\bar{C}$  adds one of the  $\alpha$  H atoms from succinic acid (1:0530): e.g.,  $\bar{C}$  with disodium succinate +  $Ac_2O$  yields an intangible intermediate which suffers two types of further change, on one hand losing  $H_2O$  to give trichloromethylparaconic acid ( $\beta$ -carboxy- $\gamma$ -trichloromethyl- $\gamma$ -butyrolactone) [Beil. XVIII-372], and on the other suffering hydrolysis of its  $-CCl_3$  group to give isocitric acid ( $\alpha$ -hydroxypropane- $\alpha,\beta,\gamma$ -tricarboxylic acid) [Beil. III-555, III<sub>2</sub>-(359)]; for details of execution of these reactions see (221).]

*With  $\alpha$ -Hydroxy Acids*

Condensation of  $\bar{C}$  (or its hydrate) with acids containing an  $\alpha$ -hydroxy group leads to the formation of products generically designated as "chloralides"; these are ether-esters comprising position-5 substitution products of the true parent 2-(trichloromethyl)-1,3-dioxolanone-4 (from  $\alpha$ -hydroxynacetic acid) and are not to be confused with the specific compound "chloralide" (3:3510) obtd. from  $\bar{C}$  with  $H_2SO_4$ . With true chloralides above the initial parent, two geometrically isomeric forms are possible.

With  $\alpha$ -hydroxyacetic acid. [ $\bar{C}$  with glycolic acid (1:0430) in a.t. at  $120-130^\circ$  for 2 days gives (224) 2-(trichloromethyl)-1,3-dioxolanone-4 ("glycolic acid chloralide") [Beil. XIX-103], m.p.  $41-42^\circ$ .]

(228), 70–71° (231), 59–60° (227); note that this disagreement of m.p.'s may be due to mixtures of possible *cis-trans* stereoisomers.)

With benzoic acid. [ $\bar{C}$  with benzoic acid (1:0770) in a.t. at 160–165° for 5 hrs. gives (231) 2-(trichloromethyl)-5,5-diphenyl-1,3-dioxolanone-4 ("benzoic acid chloralide"), m.p. 70°. Note that an analogous prod. has been reported (232) from chloral hydrate (3:1270) with thiobenzoic acid,  $(C_6H_5)_2C(SH)COOH$  in  $AcOH + HCl$  gas.]

With tartaric acid. [Since this acid is twice an  $\alpha$ -hydroxy acid it reacts with 2 moles of  $\bar{C}$  forming a dichloralide of compn.  $C_8H_4O_6Cl_2$ ; e.g.,  $\bar{C}$  with *d*-tartaric acid (1:0525) at 150° (224), or chloral hydrate (3:1270) with *d*-tartaric acid (1:0525) (227) (228) (229) (230) (231) or *d,l*-tartaric acid (1:0550) (227) (228) gives "tartaric acid dichloralide" [Beil. XIX-449], m.p. 213–215° (229); 164–166° (227), 161–162° (231), 161° (229), 160° (228), 159–161° (227); 128–130° (228), 122–124° (224), 116–118° (227). Note that this product should exist in three stereoisomeric forms (230), and the three groups of m.p.'s above given may represent this expectation.]

With mucic acid. This acid combines with 3 moles of chloral hydrate to give a prod. commonly called a "trichloralide", note, however, that it is undoubtedly a dichloralide which has further condensed at its two free OH groups with a third molecule of chloral [e.g., chloral hydrate (3:1270) with mucic acid (1:0845) +  $H_2SO_4$  gives (228) (229) a "trichloralide," m.p. 200–201° (228), 198° (229), 174–175° (229); doubtless these represent at least two stereoisomeric forms].

#### With Phenolic Acids (or Their Ethers)

In condensation of  $\bar{C}$  (or its hydrate) with phenolic acids, the latter behave like carboxy-substituted phenols; two series of products result according to whether *one* or *two* moles of carboxy-phenol are involved per mole of chloral. To assist in recognizing this analogy, the several products are here named as substituted carbinols or ethanes just as was done above in the behavior of  $\bar{C}$  with phenols (q.v.). Since the methyl ethers of these phenolic acids in general behave similarly, they are associated below with the corresponding phenolic acids.

With *o*-phenolic acids. With *o*-hydroxybenzoic acid. [Chloral hydrate (3:1270) with salicylic acid (1:0780) + conc.  $H_2SO_4$  gives (233) cf. (234) some 1,1,1-trichloromethyl-(4-hydroxy-3-carboxyphenyl)-carbinol, m.p. 180–182° (233), but main prod. is 1,1,1-trichloro-2,2-bis-(4-hydroxy-3-carboxyphenyl)ethane, m.p. 290–292° (corresp. diacetate, m.p. 207–209° (233)).]

With *o*-methoxybenzoic acid. [Chloral hydrate (3:1270) with *o*-methoxybenzoic acid (1:0685) + conc.  $H_2SO_4$  gives (yields: 45% (234), 25% (235)) 1,1,1-trichloro-(4-methoxy-3-carboxyphenyl)-carbinol, m.p. 224° (234), 216° (235), some sulfonation also occurring (235).]

With 2-hydroxy-3-methylbenzoic acid. [Chloral hydrate (3:1270) with *o*-cresotic acid [Beil. X-220, X<sub>1</sub>-(96)] + conc.  $H_2SO_4$  gives (236) 1,1,1-trichloro-2,2-bis-(4-hydroxy-3-methyl-5-carboxyphenyl)ethane, m.p. 283–285° (236); note that the corresp. carbinol to be expected from chloral hydrate + 1 mole *o*-cresotic acid is unreported.]

With 2-hydroxy-4-methylbenzoic acid. [Chloral hydrate (3:1270) with *m*-cresotic acid [Beil. X-233, X<sub>1</sub>-(100)] is complex and disputed; for discussion see (236) (237) (238) (239). — For behavior of  $\bar{C}$  with 2-methoxy-4-methylbenzoic acid see also (241).]

With 2-hydroxy-5-methylbenzoic acid. (Chloral hydrate (3:1270) with *p*-cresotic acid [Beil. X-227, X<sub>1</sub>-(98)] + conc.  $H_2SO_4$  gives (236) a prod. of compn.  $C_{12}H_8O_4Cl_2$  (2,4-bis-(trichloromethyl)-6-methyl-1,3-benzodioxin-8-carboxylic acid), m.p. 285–286° dec., derived from 2 moles chloral hydrate + 1 mole *p*-cresotic acid.)



With *2-hydroxy-3-naphthoic acid*. [For behavior of chloral hydrate (3:1270) with 2-hydroxy-3-naphthoic acid (1:0850) + conc.  $\text{H}_2\text{SO}_4$  see (242).]

With *m-phenolic acids* (or their ethers). Condensation of  $\bar{\text{C}}$  or its hydrate with *m-phenolic acids* leads generally to substituted phthalides.

With *m-hydroxybenzoic acid*. [Chloral hydrate (3:1270) with *m-hydroxybenzoic acid* (1:0825) + conc.  $\text{H}_2\text{SO}_4$  gives (243) (244) 3-(trichloromethyl)-6-hydroxyphthalide [Beil. XVIII-20], m.p. 199–200° (244), 197–198° (243). — Note that chloral hydrate (3:1270) with ethyl *m-methoxybenzoate* (1:4131) + conc.  $\text{H}_2\text{SO}_4$  gives (243) (245) 3-(trichloromethyl)-6-methoxyphthalide [Beil. XVIII-20], m.p. 135° (243) (245), which by alk. hydrolysis of the  $-\text{CCl}_3$  group gives (243) (245) 6-methoxyphthalide-3-carboxylic acid [Beil. XVIII-525], m.p. 170° (245), 169–170° (243).]

With *2-chloro-3-hydroxybenzoic acid*. [Chloral hydrate (3:1270) with 2-chloro-3-hydroxybenzoic acid (3:4395) + conc.  $\text{H}_2\text{SO}_4$  gives (246) 3-(trichloromethyl)-7-chloro-6-hydroxyphthalide, m.p. 195.5–196°.]

With *4-methyl-3-hydroxybenzoic acid*. [Chloral hydrate (3:1270) with 4-methyl-3-hydroxybenzoic acid [Beil. X-237] + conc.  $\text{H}_2\text{SO}_4$  gives (247) 3-(trichloromethyl)-5-methyl-6-hydroxyphthalide, m.p. 232° (247). — Similarly, chloral hydrate (3:1270) with 4-methyl-3-methoxybenzoic acid + conc.  $\text{H}_2\text{SO}_4$  gives (247) 3-(trichloromethyl)-5-methyl-6-methoxyphthalide, m.p. 132° (247).]

With *3,4,5-trihydroxybenzoic acid*. [Chloral hydrate (3:1270) with gallic acid (1:0876) + conc.  $\text{H}_2\text{SO}_4$  gives (236) according to conditions three different products; with excess of gallic acid prod. is 3-(trichloromethyl)-4,5,6-trihydroxyphthalide, m.p. 210–212° (236), for further reactions of which see (236) (248); with excess chloral, however, the reaction gives two other materials (236). — Note that chloral hydrate (3:1270) with 3,4,5-trimethoxybenzoic acid (gallic acid trimethyl ether) [Beil. X-481,  $\text{X}_1$ -(240)] + conc.  $\text{H}_2\text{SO}_4$  (249) (250) (251), or with methyl 3,4,5-trimethoxybenzoate (methyl gallate trimethyl ether) [Beil. X-484,  $\text{X}_1$ -(242)] (252), gives (56% yield (249)) 3-(trichloromethyl)-4,5,6-trimethoxyphthalide [Beil. XVIII-(339)], m.p. 76–77° (249), 71–72° (250), 70–71° (252) (note also that during condensation some demethylation may occur (253), avoided by (251)); this prod. by hydrolysis of the trichloromethyl group yields 4,5,6-trimethoxyphthalide-3-carboxylic acid [Beil. XVIII-(544)], m.p. 147–149° (249), 147–145° (250), 147° (251), 146–149° (254), 142–143° (252).]

With *p-phenolic acids* (or their ethers). With *p-hydroxybenzoic acid*. [Chloral hydrate (3:1270) (3 moles) with *p-hydroxybenzoic acid* (1:0840) (1 mole) + conc.  $\text{H}_2\text{SO}_4$  at room temp. for 3 days condenses giving (31% yield on the acid (255)) 2,4-bis-(trichloromethyl)benzodioxin-1,3-carboxylic acid-6, m.p. 225.5–226.5° (255); for further related reactions of this prod. see (256); for further generally similar work in benzodioxin series see (257) (258); note that neither the substituted carbinol nor the substituted ethane corresp. to the behavior of *o*-hydroxybenzoic acid (see above) under similar conditions is reported.]

With *p-methoxybenzoic acid*. [Chloral hydrate (3:1270) with *p-anisic acid* (1:0805) + conc.  $\text{H}_2\text{SO}_4$  reacts in a 1:1 ratio (note difference from 2:1 ratio in preceding paragraph) giving (259) cf. (235) trichloromethyl-(2-methoxy-5-carboxyphenyl)-carbinol, m.p. 198–199° (259); note that the earlier product (235) was impure.]

With *4-hydroxy-3,5-dimethoxybenzoic acid*. [Chloral hydrate (3:1270) with syringic acid (1:0830) + conc.  $\text{H}_2\text{SO}_4$  gives (86% yield (253)) 3-(trichloromethyl)-5-hydroxy-4,6-dimethoxyphthalide, m.p. 172–173° (253).]

With keto acids (see also below under behavior with esters of organic acids).

With *levulinic acid*. [ $\bar{\text{C}}$  (1 mole) with  $\beta$ -acetopropionic acid (levulinic acid) (1:0405)



## BEHAVIOR WITH DIAZOMETHANE

$\bar{C}$  (309) (330) (331) or chloral hydrate (3:1270) (332) gives (yields: 64% (330), 48% (309), 47.5% (332)) 3,3,3-trichloro-1,2-epoxypropene (3:5760) q.v.]

## BEHAVIOR WITH AMINES

With primary aromatic amines. With aniline.  $\bar{C}$  with aniline (333) (334), or chloral hydrate (3:1270) with aniline in aq. (334), gives 1,1,1-trichloro-2,2-dianilinoethane ( $\beta,\beta,\beta$ -trichloroethylidene)di-aniline [Beil. XII-187, XII-(168)], pr. from ether/alc., m.p. 107–108° (335), 107.5° (334), 100–101° (333). — Note that the addition product to be expected from 1 mole  $\bar{C}$  with 1 mole aniline has not itself been isolated (except as a molecular compound with chloral hydrate (336)) since it appears to react immediately with a second mole of aniline to give the above-indicated prod.]

With aniline + hydroxylamine. [Chloral hydrate (3:1270) (1 mole) with aniline (1 mole) +  $NH_2OH.HCl$  (3 moles) +  $HCl$  +  $Na_2SO_4$  in aq. solo. as directed gives (80–91% yield (337)) cf. (338) (339) isonitrosoacetanilide [Beil. XII-(275)], m.p. 175° dec. (337) (338) (339). — Note that this product with conc.  $H_2SO_4$  (337) (340) gives (71–78% yield (337)) indigo; for extension of the method to use of other amines (and ultimately substituted indigos) see (338) (341) (345).]

With other primary aromatic amines. The condensation of  $\bar{C}$  or of chloral hydrate (3:1270) with many other primary aromatic amines and diamines has been studied but cannot be detailed here [for extensive review and discussion see (336) (334) (335) (342) (343) (344) (403)].

With secondary aromatic amines. With *N*-alkylanilines. [Chloral hydrate (3:1270) with *N*-methylaniline on warming gives (346) trichloromethyl-(*p*-methylanilinophenyl)-carbinol [Beil. XIII-628], m.p. 112° dec.; similarly, chloral hydrate (3:1270) with *N*-ethylaniline on warming gives (346) trichloromethyl-(*p*-ethylaminophenyl)-carbinol [Beil. XIII-628], m.p. 98°.]

With *N*-alkyl-*o*-toluidines. [Chloral hydrate (3:1270) with *N*-methyl-*o*-toluidine +  $ZnCl_2$  gives (347) trichloromethyl-(4-methylamino-3-methylphenyl)-carbinol, m.p. 104–105°; similarly, chloral hydrate (3:1270) with *N*-ethyl-*o*-toluidine +  $ZnCl_2$  gives (349) trichloromethyl-(4-ethylamino-3-methylphenyl)-carbinol, m.p. 107° (for studies of nitration (348) and bromination (349) of these two products see indic. refs.).]

With tertiary aromatic amines. With *N,N*-dialkylanilines. [ $\bar{C}$  with *N,N*-dimethylaniline in phenol at room temp. (350) or chloral hydrate with *N,N*-dimethylaniline +  $ZnCl_2$  on stdg. (351) (352) gives trichloromethyl-(*p*-dimethylanilinophenyl)-carbinol [Beil. XIII-628], m.p. 111° dec. (352) (corresp. carbinyl acetate, m.p. 84–85° (352)) (for study of nitration of this prod. see (348)).]

## BEHAVIOR WITH ARYLEYDRAZINES

With phenylhydrazine. [ $\bar{C}$  with phenylhydrazine or chloral hydrate (3:1270) with aq. phenylhydrazine salts reacts (353) vigorously, but the products formed have not been unambiguously characterized (see also below).]

With *p*-nitrophenylhydrazine. [Chloral hydrate (3:1270) (large excess) with *p*-nitrophenylhydrazine in  $AcOH$  at 100° for 10 min. undergoes a series of reactions resulting (354) in a chlorine-free prod., m.p. 225°, regarded (354) as 1-(*p*-nitrophenyl)-3,5-dihydroxy-pyrazolone-4-(*p*-nitrophenylhydrazone).]

With 2,4-dinitrophenylhydrazine. [Chloral hydrate (3:1270) with 2,4-dinitrophenylhydrazine gives according to conditions either or both (355) glyoxylic acid *p*-nitrophenyl-

hydrazone, dihydrate from nq., m.p. 191° (355); anhydrous, m.p. 194–195° (355), 190° (356), or chloroglyoxal bis-(2,4-dinitrophenylhydrazine), m.p. 278° (355).]

With various halogenated hydrazines. Owing to the violence with which the product initially formed decomposes, the behavior of  $\bar{C}$  with phenylhydrazine (see also above) has been little studied. With halogenated phenylhydrazines the decomposition is more moderate and has been extensively examined. The nature of the products has been found to depend mainly upon the solvent medium: thus in alcohols the principal product is the corresponding substituted phenylhydrazone of the appropriate alkyl glyoxylate; in water or AcOH, however, loss of both  $H_2O$  and  $HCl$  occurs leading to formation of the corresponding  $\alpha,\alpha$ -dichloro- $\beta$ -aryldiazoethylenes.

[Chloral hydrate (1 mole) (3:1270) with 2,4-dichlorophenylhydrazine in ethyl alc. at 60° gives (100% yield (357)) ethyl glyoxylate 2,4-dichlorophenylhydrazone, yellow pr., m.p. 121.5°, note that other ales. (357) give corresp. esters. — However, chloral hydrate (1 mole) (3:1270) with 2,4-dichlorophenylhydrazine (1 mole) in AcOH at 80° (or in presence of NaOAc at 60°) gives (357)  $\alpha,\alpha$ -dichloro- $\beta$ -(2,4-dichlorobenzencazo)ethylene, red pr. from alc., m.p. 84.5°.]

[For completely analogous behavior of chloral hydrate (3:1270) with other halogenated phenylhydrazines, such as 2,5-dichlorophenylhydrazine (358), 2,4,5-trichlorophenylhydrazine (358), 2,4,6-trichlorophenylhydrazine (359), 2,4,6-tribromophenylhydrazine (359), 3-bromo-4-methylphenylhydrazine (360), or 3,5-dibromo-4-methylphenylhydrazine (360), see indie refs. — Note that a generally analogous behavior toward halogenated arylhydrazines is shown by butyrylchloral (3:5910) q.v. and by tribromoacetaldehyde (bromal).]

#### BEHAVIOR WITH AMIDES

$\bar{C}$  with compounds of the amide type readily undergoes an addition reaction leading to products of the general form  $CCl_2CH(OH).NH.CO.R$ .

##### With Aliphatic Monoamides

With formamide. [ $\bar{C}$  (1 mole) with formamide (1 mole) on stdg. gives (361) (362) an addition prod., chloralformamide,  $CCl_2CH(OH).NH.CHO$  [Beil. II-27, II<sub>1</sub>-(21), II<sub>2</sub>-(37)], m.p. 124–126° (363), 118° (362), 115–116° (361); note that this product has in the literature often been confused with the isomeric  $\beta,\beta,\beta$ -trichloroethyl carbamate,  $CCl_3-CH_2O.CO.NH_2$  ("Voluntal") [see also under  $\beta,\beta,\beta$ -trichloroethyl alcohol (3:5775)] Note also that chloralformamide with aq. NaOH +  $Ac_2O$  (362) or with aq. NaOH +  $BzCl$  (361) cf. (362) undergoes bimolecular condensation with loss of  $H_2O$  giving anhydrochloralformamide  $[CCl_2CH(NH.CHO)]_2O$ , m.p. 194.5–195° (362), 193° (364).]

With acetamide. [ $\bar{C}$  (1 mole) with acetamide (1 mole) (72) (172), or chloral hydrate (3:1270) (1 mole) with acetamide (1 mole), or chloral ammonia with  $AcCl$  or  $Ac_2O$  (128) gives chloralacetamide [Beil. II-179, II<sub>1</sub>-(81)], m.p. 158–159° (362), 158° (172), 156°–157° (72), 156° (128); this prod. with aq. NaOH +  $Ac_2O$  undergoes bimolecular loss of aq. yielding (362) cf. (369) anhydrochloralacetamide,  $[CCl_2CH(NH.CO.CH_3)]_2O$ , m.p. 212–213° (362), 207° (364). — For study of reduction of chloralacetamide see (365) (366).]

With higher monoamides. [For analogous condensation of  $\bar{C}$  with propionamide, isobutyramide, n-valeramide, n-caproamide, n-caprylamide, and phenylacetamide together with study of reduction of the several products see (367) cf. (369).]

##### With Aromatic Monoamides

With benzamide. [ $\bar{C}$  (1 mole) with benzamide (1 mole) (172) (362) cf. (369), or chloral hydrate (3:1270) with benzonitrile + dry  $HCl$  (368) gives chloralbenzamide [Beil. IX-

209, IX<sub>1</sub>-(101)], m.p. 150–151° (72), 150° (362), 146° (172) (368); this product with aq. NaOH + BzCl or Ac<sub>2</sub>O gives (362) by dehydrative bimolecular condensation anhydrochloralbenzamide, known (362) in two forms, higher-melting form, m.p. 199–200°, and lower-melting form, m.p. 137–138°. — For study of reduction of chloralbenzamide see (366) cf. (369).]

With toluamides. [For condensation of  $\bar{C}$  with *o*-, *m*-, and *p*-toluamides see (370); for the behavior of the products with PCl<sub>5</sub> see (371).]

With salicylamide. [ $\bar{C}$  with salicylamide on warming directly (372) or in CHCl<sub>3</sub> (373) gives chloralsalicylamide, entering at 117° and melting about 10° higher (372); for the corresp. anhydro compound (cf. above), m.p. 174–175°, see (369); for studies of chloral-salicylamide on chlorination (374), bromination (375), or nitration (375) see indic. refs.]

With amides of various substituted salicylic acids. [For behavior of  $\bar{C}$  with the amides of 3-chlorosalicylic acid (3:4745), 5-chlorosalicylic acid (3:4705), and 3,5-dichlorosalicylic acid (3:4035) see (374) (376) (377); for behavior of  $\bar{C}$  with amides of various nitrosalicylic acids (378) or various aminosalicylic acids (379) see indic. refs.]

With *o*-aminobenzamide (anthranilamide). [For behavior of  $\bar{C}$  with anthranilamide and its relatives see (380).]

#### With Amides of Dibasic Acids

Note that two series of products are formed.

With urea. [Chloral hydrate (3:1270) (1 mole) with urea (2 moles) in aq. soln. on stdg. 3 days at room temp. gives (66% yield (381)) (382) cf. (172) chloralurea, *N*-( $\beta,\beta,\beta$ -trichloro- $\alpha$ -hydroxyethyl)urea [Beil. III-59, III<sub>1</sub>-(27)], cryst. from MeOH/C<sub>6</sub>H<sub>6</sub> (381) or EtOH/C<sub>6</sub>H<sub>6</sub> 1:3 (382), m.p. 150° dec. (381) (382). — However, chloral hydrate (3:1270) (2 moles) with urea (1 mole) in aq. HCl at room temp. for 3 days gives (71% yield (381)) (382) cf. (383) dichloralurea [Beil. III-60, III<sub>1</sub>-(27), III<sub>2</sub>-(40)], cryst. from aq. alc., m.p. 196° (381), 194° dec. (382), 190° (172).]

With thiourea. [For behavior of  $\bar{C}$  with thiourea see (383).]

With various substituted ureas. *With monosubstituted ureas.* [Chloral hydrate (3:1270) (2 moles) with *N*-methylurea (1 mole) in aq. soln. at room temp. gives (384) *N*-methyl-*N'*-( $\beta,\beta,\beta$ -trichloro- $\alpha$ -hydroxyethyl) urea, m.p. 140° dec. (384). — Chloral hydrate (3:1270) with *N*-ethylurea behaves in analogous fashion (384). — Chloral hydrate (3:1270) (2½ moles) with *N*-phenylurea in aq. HCl gives (84% yield (382)) *N*-phenyl-*N'*-( $\beta,\beta,\beta$ -trichloro- $\alpha$ -hydroxyethyl)urea, m.p. 142° dec. (382). — For corresp. behavior of chloral hydrate (3:1270) with *N*-*o*-tolylurea, *N*-*p*-tolylurea, *N*-*m*-nitrophenylurea, and *N*-*p*-nitrophenylurea see (385).]

*With disubstituted ureas.* [Chloral hydrate (3:1270) with *N,N*-dimethylurea gives (384) cf. (386) *N,N*-dimethyl-*N'*-( $\beta,\beta,\beta$ -trichloro- $\alpha$ -hydroxyethyl)urea, cryst. from aq. as monohydrate, m.p. 74° dec. (384) (386), which becomes anhydrous on stdg., cryst. from alc., m.p. 157° dec. (384), 156° (386). — For analogous behavior of  $\bar{C}$  with *N,N*-diethylurea giving prod., m.p. 146° dec. (384), 142° (386), see indic. refs. —  $\bar{C}$  with *N,N*-diphenylurea gives analogous prod., m.p. 170° dec. (384).]

With amides of other dibasic acids. [For generally analogous behavior of  $\bar{C}$  with oxamide (384), malonamide (384) (369), succinamide (369), and their relatives see indic. refs.]

#### With Urethanes

With ethyl carbamate. [ $\bar{C}$  with ethyl carbamate ("urethane") in conc. HCl gives (387) (388) ethyl *N*-( $\beta,\beta,\beta$ -trichloro- $\alpha$ -hydroxyethyl)carbamate ("chloralurethane") [Beil. III-24, III<sub>1</sub>-(12), III<sub>2</sub>-(22)], m.p. 103° (362) (388). — This product on htg. alone or

in aq. at 100° regenerates (388) chloral and ethyl carbamate. — With AcCl under reflux it gives (80% yield (387)) the corresp. acetate, m.p. 47–49°, b.p. 165° at 15 mm. (387). — With aq. NaOH + Ac<sub>2</sub>O (362) (387) or with aq. KOH + BzCl (364) chloralurethane undergoes dehydrative bimolecular condensation yielding anhydro-chloralurethane [Beil. III<sub>1</sub>-12], which exists in both high-melting (161–162°) and low-melting (149–150°) forms (362).]

With other alkyl carbamates. [For generally analogous behavior of  $\bar{C}$  with methyl carbamate (362), *n*-propyl carbamate (389), isobutyl carbamate (389), isoamyl carbamate (362), and menthyl carbamate (362) see indic. refs.]

Ⓢ Preliminary tests for  $\bar{C}$ : Owing to the length of the text of this compound, a brief summary of the tests most significant as preliminary indications is given here; for details refer back as indicated and also see chloral hydrate (3:1270).

$\bar{C}$  reduces NH<sub>3</sub>/AgNO<sub>3</sub> and Fehling's soln. but only on warming (see above under oxdn of  $\bar{C}$ ). —  $\bar{C}$  gives fuchsin-aldehyde test with Schiff's reagent (but chloral hydrate (3:1270) does not). —  $\bar{C}$  with conc. H<sub>2</sub>SO<sub>4</sub> readily polymerizes (see above under polymerization of  $\bar{C}$ ). —  $\bar{C}$  with aq. or alc. alkali on warming undergoes hydrolytic cleavage to CHCl<sub>3</sub> (3:5050) + alkali formate (see above under behavior of  $\bar{C}$  with alkalis); therefore,  $\bar{C}$  with alc. alkali + aniline gives characteristic odor of phenyl isocyanide.

— Trichloroacetalaldioxime: m.p. 56° (135). [See above under behavior of  $\bar{C}$  with hydroxylamine.]

— Trichloroacetaldehyde phenylhydrazone: unreported. [See above under behavior of  $\bar{C}$  with arylhydrazines.]

— Trichloroacetaldehyde *p*-nitrophenylhydrazone: unreported. [See above under behavior of  $\bar{C}$  with arylhydrazines.]

— Trichloroacetaldehyde 2,4-dinitrophenylhydrazone: a prod. of m.p. 131° has been claimed (390) but could not be confirmed (391). [See also above under behavior of  $\bar{C}$  with arylhydrazines.]

— Trichloroacetaldehyde semicarbazone: unreported. [Note that chloral hydrate (3:1270) with semicarbazide in aq. (392) (394) cf. (393) or chloral ethylalcoholate (3:0860) with semicarbazide in alc. (392) gives an addn. prod., m.p. 90°, which on boilg. with aq. yields (392) glyoxylic acid semicarbazone [Beil. III-600, III<sub>1</sub>-(209) III<sub>2</sub>-(389)], m.p. 235–236° (392), 235–238° (393), 207° (395), 206–208° dec. (396), 202–203° (397), 202° dec. (394) (note that these results may represent two stereoisomeric forms (397)).]

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2103, 2104, 2105, 2106, 2107, 2108, 2109, 2110, 2111, 2112, 2113, 2114, 2115, 2116, 2117, 2118, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2126, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2142, 2143, 2144, 2145, 2146, 2147, 2148, 2149, 2150, 2151, 2152, 2153, 2154, 2155, 2156, 2157, 2158, 2159, 2160, 2161, 2162, 2163, 2164, 2165, 2166, 2167, 2168, 2169, 2170, 2171, 2172, 2173, 2174, 2175, 2176, 2177, 2178, 2179, 2180, 2181, 2182, 2183, 2184, 2185, 2186, 2187, 2188, 2189, 2190, 2191, 2192, 2193, 2194, 2195, 2196, 2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205, 2206, 2207, 2208, 2209, 2210, 2211, 2212, 2213, 2214, 2215, 2216, 2217, 2218, 2219, 2220, 2221, 2222, 2223, 2224, 2225, 2226, 2227, 2228, 2229, 2230, 2231, 2232, 2233, 2234, 2235, 2236, 2237, 2238, 2239, 2240, 2241, 2242, 2243, 2244, 2245, 2246, 2247, 2248, 2249, 2250, 2251, 2252, 2253, 2254, 2255, 2256, 2257, 2258, 2259, 2260, 2261, 2262, 2263, 2264, 2265, 2266, 2267, 2268, 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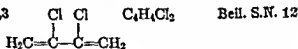
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## 3:5220 2,3-DICHLOROBUTADIENE-1,3



B.P. 98° at 760 mm. (1) (2)  
 41-43° at 85 mm. (1)  
 40-43° at 85 mm. (3)

$D_4^{20} = 1.1829$  (1)  $n_D^{20} = 1.4800$  (1)

[For prepn. of  $\bar{C}$  (86% yield (1)) from 1,2,3-trichlorobutene-3 (2,3,4-trichlorobutene-1) (3:9964) with excess MeOH/KOH at 10-15° see (1) (2); for formn. (together with other products) from 1,2,3,4-tetrachlorobutane (3:1760) with MeOH/KOH at 10-18° see (1) (2); from chloroprene (3:7080) by addn. of ICl followed by treatment with alc. KOH (3:1)  $\bar{C}$  polymerizes completely within 24 hrs. at room temp., in about 49 min. at 85-90°; this is about 10 times as fast as chloroprene (3:7080) and 7000 times as fast as isoprene (1:8020). The polymer is a white opaque tough hard mass, non-plastic and lacking extensibility. It is insol. in and separates from liquid  $\bar{C}$  but is partly soluble in  $\text{CHCl}_3$  (1). The polymerization is inhibited by hydroquinone and accelerated by benzoyl peroxide (2).  $\bar{C}$  does not (1) react with maleic anhydride (1:0625) or with 1,4-naphthoquinone (1:9040).

3:5226 (1) Carothers, Berchet, *J. Am. Chem. Soc.* 55, 2004-2008 (1933). (2) Carothers, Berchet, U.S. 1,965,319, July 3, 1934; *Cent.* 1935, I 3724; C.A. 28, 5716 (1934). (3) Petrov, *J. Gen. Chem. (U.S.S.R.)* 13, 155-158 (1943); C.A. 38, 1466-1467 (1944).



[For prepn. of  $\bar{C}$  from chloroacetic acid (3:1370) with  $PCl_3$  (5) (40), or in  $HCl$  atm. under press. nt  $150^\circ$  (6), or with  $ZnCl_2$  (67% yield (7)) see indic. refs.; with  $P_2O_5 + HCl$  gas nt  $200^\circ$  see (8); with  $SOCl_2$  (yields: 95% (9), 55% (10), 50% (7)) (11) see indic. refs.; with benzoyl chloride (3:6240) (yield 71-76%) see (12); with oxalyl dichloride (3:5060) (80% yield) see (3); with phosgene (3:5000) over activated carbon nt  $200^\circ$  see (13); with benzotrichloride (3:6540) +  $ZnCl_2$  at  $80-90^\circ$  (80% yield) see (14); with  $Cl_2 + S_2Cl_2$  (95% yield (15)) or  $Cl_2 +$  lower chlorides of sulfur +  $FeCl_3$ ,  $SnCl_4$ , etc., at  $50-60^\circ$  (82% yield (16)) see indic. refs.]

[For prepn. of  $\bar{C}$  from chloroacetic acid anhydride (3:0730) with oxalyl dichloride (3:5060) see (3); from ketene with  $NOCl$  see (17); from  $\alpha,\beta$ -dichlorovinyl ethyl ether (3:5540) +  $HCl$  gas see (18); from  $\alpha,\beta$ -dichloroethylene +  $O_2$  in pres. of  $Br_2$  or conc.  $H_2SO_4$  see (19); from nectyl chloride (3:7065) with  $Cl_2$  in sunlight (20) or in  $CCl_4$  in u.v. light (21) or in pres. of  $I_2$  (22) see indic. refs.; from  $\alpha$ -chloroethyl chloroacetate on htg. with 0.02%  $ZnCl_2$  see (23); from 2-(chloroacetoxy)hexene-1 with  $HCl$  gas see (24), from  $CH_3Cl_2$  (3:5020) +  $AlCl_3$  +  $CO$  gas at  $200^\circ$  and 900 atm. see (41).]

$\bar{C}$  on htg. with  $Na_2CO_3$  (25) or with  $KNO_3$  (81% yield (26)) gives chloroacetic acid anhydride (3:0730) q.v., m.p.  $46^\circ$ . —  $\bar{C}$  treated at  $-5^\circ$  with  $III$  gas gives (68% yield (27)) chloroacetyl iodide, b.p.  $36.5^\circ$  at 4 mm. (27). [For behavior of  $\bar{C}$  with  $HBr$  gas see (40).]

$\bar{C}$  with  $MeOH$  yields (28) methyl chloroacetate (3:5585), b.p.  $131^\circ$ ;  $\bar{C}$  with  $EtOH$  (29) or with triethyl orthoformate (1:3241) at  $100-110^\circ$  (90% yield (30)) gives ethyl chloroacetate (3:5700), b.p.  $144^\circ$ .

[ $\bar{C}$  with ethylene +  $AlCl_3$  gives (small yield (31)) 1,4-dichlorobutanone-2, b.p.  $63-65^\circ$  at 3 mm. (31). —  $\bar{C}$  with  $C_6H_6$  +  $AlCl_3$  gives (32)  $\omega$ -chloroacetophenone (phenacyl chloride) (3:1212);  $\bar{C}$  with *m*-dichlorobenzene (3:5960) +  $AlCl_3$  gives (33) 2,4-dichlorophenacyl chloride [Beil. VII-283], m.p.  $57^\circ$  (33);  $\bar{C}$  with biphenyl +  $AlCl_3$  gives (77% yield (34)) *p*-phenylphenacyl chloride (3:3934), m.p.  $122-123^\circ$  (34);  $\bar{C}$  with naphthalene +  $AlCl_3$  in  $CS_2$  gives (35) cf. (36) chloromethyl  $\beta$ -naphthyl ketone.]

[ $\bar{C}$  with large excess (4 moles)  $McMgBr$  or  $McMgI$  gives (48-51% yield (37)) (38) 2-methylbutanol-3 (1:6170);  $\bar{C}$  with large excess  $CaH_2MgBr$  in ether gives (31% yield (39)) 1,2,2-triphenylethanol-1 [Beil. VI-721], m.p.  $87.5-88.5^\circ$  (39); note that the isomeric 1,1,2-triphenylethanol-1 [Beil. VI-(354)] has almost same m.p., viz.,  $89^\circ$ .]

$\bar{C}$  hydrolyzes with aq. yielding chloroacetic acid (3:1370) q.v. — For the amide, anilide, *p*-toluidide, and other deriva. corresp. to  $\bar{C}$  see chloroacetic acid (3:1370).

3:5235 (1) Martin, Partington, *J. Chem. Soc.* 1936, 162. (2) Cheng, Z. *physik. Chem.* B-26, 295 (1934). (3) Adams, Ulrich, *J. Am. Chem. Soc.* 42, 604, 606 (1920). (4) Vanderstichele, *J. Chem. Soc.* 123, 1228 (1923). (5) do Wilde, *Ann.* 130, 372-373 (1861). (6) Scheuble, *Ger.* 251,806, Oct. 8, 1912; *Cent.* 1912, II 1503-1504. (7) Clark, Bell, *Trans. Roy. Soc. Canada* (3) 27, III 97-103 (1933). (8) Frankland, Patterson, *J. Chem. Soc.* 73, 100 (1898). (9) Barnett, *Chem. News* 122, 220-221 (1921); *Cent.* 1921, III 463. (10) McMaster, Ahmann, *J. Am. Chem. Soc.* 50, 146 (1928).

(11) Bödesken, *Rec. trav. chim.* 33, 5 (1913). (12) Brown, *J. Am. Chem. Soc.* 60, 1325-1328 (1938). (13) Hochstetter, *Ger.* 283,896, April 27, 1915; *Cent.* 1915, I 1190. (14) Rabcewicz-Zubkowski, *Roczniki Chem.* 9, 526-527 (1929); *Cent.* 1929, II 2767; *C.A.* 24, 61 (1930). (15) Read, *J. Am. Chem. Soc.* 44, 1751 Note (1922). (16) Britton (to Dow Chem. Co.), U.S. 1,805,162, May 12, 1931; *Cent.* 1931, II 631; *C.A.* 25, 3670 (1931). (17) Deakin, Wilsmore, *J. Chem. Soc.* 97, 1977 (1910). (18) Consortium für Elektrochem. Ind., *Ger.* 222,194, May 10, 1910; *Cent.* 1910, I 1999. (19) Consortium für Elektrochem. Ind., *Ger.* 340,872, Sept. 10, 1921; *Cent.* 1921, IV 1101. (20) Wurtz, *Ann. chim.* (3) 49, 60 (1857).

(21) Benrath, Hertel, Z. *wiss. Phot.* 23, 35 (1924). (22) Jazukowitsch, *Zeit. für Chemie* 1868, 234. (23) Soc. Usines C. 1611. (24) Slanina, *Be* 211-212 (1905). (26) D

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3:5245	sym-DICHLORODIMETHYL ETHER (bis-(Chloromethyl) ether)	$C_2H_4OCl_2$ $ClCH_2O.CH_2Cl$	Beil. I - 582 I <sub>1</sub> -(305) I <sub>2</sub> -(646)
B.P. 105°	(1) (2) (8)	$D_4^{20} = 1.315$ (1)	$n_D^{21} = 1.435$ (2)
104-100°	(3)	$D_4^{15} = 1.328$ (2)	
103-106°	(4)		

Liq. fums. in moist air.

$\bar{C}$  dis. slowly in cold and rapidly in warm aq. owing to hydrolysis to formaldehyde (1:0145) + HCl. [For quant. study see (5).]

[For prepn. from formalin (1:0145), paraformaldehyde (1:0080) (95% yield (6)), or hexamethylenetetramine + chlorosulfonic ac. + conc.  $H_2SO_4$  see (6) (7); from paraformaldehyde (1:0080) + conc.  $H_2SO_4$  + HCl gas (85% yield (8)) see (8); for prepn. from dimethyl ether by chlorination see (9) (10).]

[For use in production of halogenated higher ethers by addn. to olefins see (11).]

- 3:5245 (1) Regnault, *Ann.* 34, 31 (1840). (2) Brochet, *Ann. chim.* (7) 10, 297 (1897). (3) Grassi, Maselli, *Gazz. chim. ital* 28, 11 485 (1898). (4) Litterschied, *Ann.* 330, 116 (1903). (5) Böhm, *Ber.* 74, 248-256 (1911), C.A. 35, 3972-3973 (1941). (6) Böhm, *J. Chem. Soc.* 117, 513-515 (1920). (7) Carr, *J. Soc. Chem. Ind.* (8) Salzb, *Angew. Chem.* 51, 271 (1938). (9) Salzb, *Wernitz (to du Pont Co.)* U.S. 2,066,905, Jan. 5, 1937, C.A. 31, 1037 (1937); *Cent.* 1937, 1 3529. (10) Booth (to du Pont Co.) U.S. 2,024,749, Dec. 17, 1935, Brit. 423,520, C.A. 30, 1067 (1936); C.A. 29, 4374 (1935).

3:5270	1,1,1-TRICHLOROPROPANE ("Ethylchloroform")	$CH_3CH_2CCl_3$ $C_2H_5Cl_3$	Beil. S.N. 10
B.P. 106.5-108.5°	(1)	$D_4^{25} = 1.287$ (1)	
106-107°	(1) (2)		

[For prepn. from 1,1-dichloropropene-I (3:5129) + HCl +  $AlCl_3$  at 5-10° see (1) (2) (3).]

[The compd. listed in Beil. I-106 as  $\bar{C}$  is erroneous (1) (3).]

- 3:5270 (1) Levine, *Can. J. Chem.* 31, 1572 (1953). (2) Levine, *Can. J. Chem.* 31, 1572 (1953). (3) Van Arkel, *Rec. trav. chim.* 51, 1572 (1952).

**3:5275 CHLOROMETHYL CHLOROFORMATE**  $\text{C}_2\text{H}_2\text{O}_2\text{Cl}_2$  Beil. III —  
 (Chloromethyl chlorocarbonate)  $\text{ClCH}_2\text{—O—C(=O)Cl}$  III<sub>1</sub>-(6)  
 III<sub>2</sub>-(11)

B.P. 106.5–107° at 760 mm. (1)  $D_{25}^{25} = 1.465$  (1)  $n_D^{22} = 1.4286$  (2)  
 107° (8)  
 106.5° (2)  
 104–107° (3)  $D_{25}^{25} = 1.456$  (2)  
 52.5–53° at 100 mm. (1)

See also text.

[See also dichloromethyl chloroformate (3:5315).]

Colorless lachrymatory oil. — Note that  $\bar{\text{C}}$  cannot by distillation be completely separated from dichloromethyl chloroformate (3:5315); the constants listed above are on samples contg. (1) about 9% of the latter, or (3) about 7% of dichloromethyl chloroformate + 2% dimethyl carbonate.

A mixt. of  $\bar{\text{C}}$  with dichloromethyl chloroformate (3:5315) has been employed as a chem. warfare agent under the names "K-Stoff," "Palite" (6). — [For studies of physiological action see (4) (5); for action on plant tissue see (7).]

[For prepn. of  $\bar{\text{C}}$  from methyl chloroformate (3:5075) or from methyl formate (1:1000) with  $\text{Cl}_2$  under various conditions see (1) (2) cf. (6) (8) (9).]

$\bar{\text{C}}$  with aq. at ord. temp. or more rapidly on boilg. or  $\bar{\text{C}}$  with aq. alk. in cold undergoes hydrolysis (1) yieldg formaldehyde (1:0145) + 2 HCl +  $\text{CO}_2$ ; by detn. via oxidn. with  $\text{I}_2$  + NaOH of the formaldehyde so produced  $\bar{\text{C}}$  may be quant. estimated cf. (10) (6); note also that this hydrolysis to formaldehyde distinguishes  $\bar{\text{C}}$  from various other closely related compounds, e.g., methyl chloroformate (3:5075), dichloromethyl chloroformate (3:5315), trichloromethyl chloroformate ("Diphosgene") (3:5515), trichloromethyl trichloroacetate (3:0290), bis-(trichloromethyl) carbonate ("Triphosgene") (3:1915), or phosgene (3:5000).

$\bar{\text{C}}$  (1 mole) with NaI (2 moles) in dry acetone at 20° (11) liberates  $\text{I}_2$  also yieldg formaldehyde (1:0145) + CO, but the reaction is not quantitative proceeding only to about 70% theoretical (11); but  $\bar{\text{C}}$  with dry NaI at 90–100° gives (1) CO +  $\text{CO}_2$ . Note that  $\bar{\text{C}}$  with LiBr in dry acetone does not (11) liberate bromine; in this respect  $\bar{\text{C}}$  is like methyl chloroformate (3:5075) but different from dichloromethyl chloroformate (3:5315) and trichloromethyl chloroformate ("Diphosgene") (3:5515).

[ $\bar{\text{C}}$  with  $\text{FeCl}_3$  or  $\text{AlCl}_3$  dec. rapidly at 70° (1) (12) yieldg phosgene (3:5000) and formaldehyde (1:0145).]

[ $\bar{\text{C}}$  with methyl hydrogen sulfate gives (13) methyl chlorosulfonate, formaldehyde,  $\text{CO}_2$  + HCl;  $\bar{\text{C}}$  with chlorosulfonic acid at 100° for 4 hrs. gives (13) chloromethyl chlorosulfonate +  $\text{CO}_2$  + HCl;  $\bar{\text{C}}$  with dimethyl sulfate gives (78% yield (13)) methyl chlorosulfonate.]

[ $\bar{\text{C}}$  with alcohols or  $\bar{\text{C}}$  with alkali salts of phenols reacts as an acid chloride yielding (6) the corresp. alkyl or aryl chloromethyl carbonates (1).]

[ $\bar{\text{C}}$  with K phenylcyanamide also reacts as an acid chloride givg (14) chloromethyl N-cyano-N-phenylcarbamate, m.p. 48°.]

3:5275 (1) Kling, Florentin, Lassieur, Schmutz, *Compt. rend.* 169, 1046–1047 (1919); *Ann. chim.* (9) 13, 44–59 (1920). (2) Grignard, Rivat, Urbain, *Compt. rend.* 169, 1074–1077 (1919); *Ann. chim.* (9) 13, 246–248 (1920). (3) Herbst, *Kolloidchem. Beihefte*, 23, 330–331 (1927). (4) van Nieuwenberg, *Chem. Weekblad* 19, 328 (1922). (5) Fegler, *Compt. rend. soc. biol.* 100, 222–224





[For use as soil disinfectant of the mixt. of  $\bar{C}$  with 1,2-dichloropropene obtd. in manufacture of allyl chloride by chlorination of propylene see (15); for use of  $\bar{C}$  in prepn. of cellulose ethers see (16).]

Reactions involving unsaturated linkage of  $\bar{C}$ . [ $\bar{C}$  with  $Cl_2$  adds 1 mole halogen yielding (14) 1,1,2,3-tetrachloropropane (3:6035), b.p. 179–180° cor. st 756.6 mm. (14).] —  $\bar{C}$  with  $Br_2$  adds 1 mole halogen giving (72.7% yield (9)) (5) (3) (17) 1,2-dibromo-1,3-dichloropropane [Beil. I-112], b.p. 212° (3), 215–217° (9), 220–221° (17), 220–225° (5).

[ $\bar{C}$  with fuming  $HCl$  in s.t. at 150° blackens but does not add  $HCl$  (5).]

Reactions involving the one reactive chlorine atom of  $\bar{C}$ . Note that the 2 chlorine atoms in  $\bar{C}$  possess very different reactivities; that attached to the carbon directly connected with the double bond is inert, while the chlorine attached to the carbon in  $\beta$ -relationship to the unsaturated linkage is extremely reactive.

[ $\bar{C}$  with aq.  $KOH$  (1 mole) boiled for 30 hrs. (14), or boiled with 10% aq.  $Na_2CO_3$  (slight excess) for 2 hrs. (1), or shaken with aq. silver oxide at room temp. for 24 hrs. (small yield (12)) gives 3-chloropropen-2-ol-1 (1-chloropropen-1-ol-3) ( $\gamma$ -chloroallyl alcohol) (3:5820); note that the high-boilg. stereoisomer of  $\bar{C}$  gives (76% yield (1)) the high-boilg. stereoisomer of the resultant alc., while the low-boilg. stereoisomer of  $\bar{C}$  gives (81% yield (1)) the low-boilg. stereoisomer of the resultant alc.; note also that aq.  $NaOH$  effects from the resultant  $\gamma$ -chloroallyl alc. the removal of  $HCl$  and also causes polymerization (1) so that use of hydrolytic conditions as mild as possible is desirable.] — [For reactn. of  $\bar{C}$  with  $NaSH$  or  $Na_2S$  see (18).]

[ $\bar{C}$  with  $Na$  alcoholates,  $NaOR$ , replaces the reactive chlorine atom by the alkoxy residue yielding  $\omega$ -chloroallyl alkyl ethers of general formula  $RO-CH_2-CH=CHCl$ : e.g.,  $\bar{C}$  with  $NaOMe$  refluxed 4 hrs. gives (12) 1-chloro-3-methoxypropene-1, b.p. 107–108°,  $D_4^{27} = 1.032$ ,  $n_D^{27} = 1.431$  (12) (note proximity of h.p. to that of ord.  $\bar{C}$ ) (for study of kinetics of this reactn. see (19));  $\bar{C}$  with  $NaOEt$  refluxed for 4 hrs. (12) or  $\bar{C}$  with alc.  $KOH$  (5) yields 1-chloro-3-ethoxypropene-1 [Beil. I-439], b.p. 126–127°,  $D_4^{16} = 1.018$ ,  $n_D^{16} = 1.438$  (12); for corresp. reactns. of  $\bar{C}$  with  $Na$  derivs. of benzyl alc. (1:6480),  $\beta$ -phenylethyl alc. (1:6505),  $\gamma$ -phenyl- $n$ -propyl alc. (1:6520), and cinnamyl alc. (1:5920) together with physical consts. of prods. see (20).]

[ $\bar{C}$  with alkali metal phenolates replaces the reactive chlorine atom by the aryloxy residue yielding  $\omega$ -chloroallyl aryl ethers of general formula  $RO-CH_2-CH=CHCl$ : e.g.,  $\bar{C}$  with  $Na$  phenolate in abs. alc. refluxed  $\frac{1}{2}$  hr. (21), or  $\bar{C}$  with phenol (1:1420) + dry  $K_2CO_3$  in boilg. acetone (8), gives (yields: 75% (21), 72% (8))  $\omega$ -chloroallyl phenyl ether, b.p. 120–121° at 20 mm. (21), 122–127° at 27 mm. (8),  $D_4^{15} = 1.146$  (21),  $n_D^{20} = 1.5421$  (8),  $n_D^{15} = 1.5447$  (21); for corresp. reactn. with salts of  $o$ -cresol (1:1400) (21),  $m$ -cresol (1:1730) (21),  $p$ -cresol (1:1410) (21) (8), carvacrol (1:1760) (21), thymol (1:1430) (21),  $\beta$ -naphthol (1:1540) (21), hydroquinone (1:1590) (21), and several other phenols (21) see indie. refs. — Note that these  $\omega$ -chloroallyl aryl ethers upon treatment with  $Br_2$  do not add halogen to the unsatd. linkage but instead undergo cleavage: e.g.,  $\omega$ -chloroallyl phenyl ether (above) in  $CHCl_3$  with  $Br_2$  (1 mole) at 0° yields (22) phenol (1:1420) +  $p$ -bromophenol + 3-bromo-1-chloropropene-1 (see below) +  $\omega$ -chloroallyl  $p$ -bromophenyl ether, b.p. 153° at 13 mm.,  $D_4^{11} = 1.521$ ,  $n_D^{11} = 1.5785$  (22). — Note furthermore that these  $\omega$ -chloroallyl aryl ethers with  $HBr$  or  $HI$  do not add hydrogen halide to the unsaturated side chain but instead undergo cleavage similar to that with halogens: e.g.,  $\omega$ -chloroallyl phenyl ether in  $AcOH$  with  $HBr$  gas (1 mole) gives (70% yield (23)) 3-bromo-1-chloropropene-1, lachrymatory oil, b.p. 130° at 760 mm.,  $D_4^{25} = 1.670$ ,  $n_D^{25} = 1.5255$  (23); similarly action of  $HI$  yields (23) 1-chloro-3-iodopropene-1, lachrymatory oil, b.p. 162° at 760 mm. sl. dec., 58° at 19 mm.,  $D_4^{25} = 2.029$ ,  $n_D^{25} = 1.5993$  (23).]

[ $\bar{C}$  with phenols under suitable conditions can also react to effect direct nuclear alkenyla-

tion: e.g.,  $\bar{C}$  with phenol (1:1420) + Na in  $C_6H_6$  refluxed for 17 hrs. gives (17% yield (8)) *o*-( $\gamma$ -chloroallyl)phenol, b.p. 151–156° at 31 mm.,  $n_D^{25} = 1.5638$  (8) (soluble in alk.), accompanied by some  $\omega$ -chloroallyl phenyl ether (insol. alk.) (see above).]

[ $\bar{C}$  with phenol ethers undergoes Friedel-Crafts reactn. of the reactive halogen atom with resultant introduction of the  $\omega$ -chloroallyl group into the aromatic nucleus: e.g.,  $\bar{C}$  (1 mole) with anisole (1:7445) (10 moles) +  $AlCl_3$  gives (70% yield (24)) 1-( $\omega$ -chloroallyl)-4-methoxybenzene, h.p. 126° at 15 mm. (24);  $\bar{C}$  (1 mole) with pyrocatechol dimethyl ether (veratrole) (1:7560) (2 moles) + Zn dust (1 g.) ( $AlCl_3$  unsuitable) gives 1-( $\omega$ -chloroallyl)-3,4-dimethoxybenzene, b.p. 162° at 15 mm.,  $D_4^{14} = 1.168$ ,  $n_D^{14} = 1.551$  (24);  $\bar{C}$  with pyrogallol trimethyl ether (1:7145) similarly yields 1-( $\omega$ -chloroallyl)3,4,5-trimethoxybenzene, b.p. 174° at 15 mm.,  $D_4^{18} = 1.176$ ,  $n_D^{18} = 1.539$  (24). — Note that such  $\omega$ -chloroallyl aryl ethers (1 mole) upon treatment with KOH (3 moles) in an alcohol  $R'.OH$  (5 moles) give (by reactn. of the  $\omega$ -chlorine and rearr. or vice versa) substituted cinnamyl ethers of the type  $RO.C_6H_4.CH=CH.CH_2OR'$ , used for prepn. of various natural prods. (24).]

[ $\bar{C}$  with aromatic hydrocarbons undergoes Friedel-Crafts reactn. of the reactive halogen atom with resultant introduction of the  $\omega$ -chloroallyl group into the aromatic nucleus e.g.,  $\bar{C}$  with  $C_6H_6$  +  $AlCl_3$  yields (25)  $\gamma$ -chloroallylbenzene (1-chloro-3-phenylpropene-1) (3:8737) (see below); for analogous reactions of  $\bar{C}$  with toluene (1:7405), *o*-xylene (1:7430), *m*-xylene (1:7420), *p*-xylene (1:7415), ethylbenzene (1:7410), cumene (1:7440), pseudocumene (1:7470), mesitylene (1:7455), *p*-cymene (1:7505), etc., see (25). — Note that the resultant  $\gamma$ -chloroallyl hydrocarbons add  $Br_2$  normally (26) to the unsatd. linkage (diff. from  $\omega$ -chloroallyl aryl ethers (above) which undergo cleavage); e.g.,  $\gamma$ -chloroallylbenzene (above) with  $Br_2$  gives  $\gamma$ -chloro- $\beta,\gamma$ -dibromo-*n*-propylbenzene, h.p. 160° at 12 mm.,  $D_4^{10} = 1.727$ ,  $n_D^{10} = 1.611$  (26) (for use of this prod. in prepn. of hydrocinnamaldehyde (1:0225) see (35).)]

[The direct actn. of  $\bar{C}$  with  $NH_3$  appears to be unreported; however,  $\bar{C}$  with KSCN followed by alk. hydrolytic cleavage is claimed (27) to yield the expected  $\gamma$ -chloroallylamine. —  $\bar{C}$  with methylamine (3 moles) in  $C_6H_6$  gives (53% yield (28)) *N*-methyl- $\gamma$ -chloroallylamine [Beil. IV<sub>2</sub>-(668)], h.p. 125° (B.PkOH, m.p. 91° (28)), accompanied by a little *N*-methyl- $\beta$ -( $\gamma$ -chloroallyl)amine [Beil. IV<sub>2</sub>-(668)], b.p. 88° at 16 mm. (28). —  $\bar{C}$  with diethylamine reacts vigorously and on making alkaline gives (75% yield (29)) (12) *N,N*-diethyl- $\gamma$ -chloroallylamine [Beil. IV<sub>2</sub>-(668)], b.p. 57–58° at 17 mm. (12), 55° at 9 mm. (29) (B.HCl, pl. from acetone, m.p. 221° (29); B.PkOH, ndls. from aq., m.p. 78° (29), 91° (12); B. $H_2PtCl_6$ , m.p. 169–170° (12)). — For reactns. of  $\bar{C}$  with tertiary amines, e.g., with  $Me_3N$  (29),  $Et_3N$  (29), or pyridine (19), see indic. refs.]

[ $\bar{C}$  (1 mole) with aniline (2 moles) in  $C_6H_6$  under reflux ppts. aniline hydrochloride and from the solvent gives (68% yield (30)) *N*-phenyl- $\gamma$ -chloroallylamine, b.p. 137° at 13 mm.,  $D_4^{13} = 1.1456$ ,  $n_D^{13} = 1.590$  (30); for analogous reactns. of  $\bar{C}$  with *o*-toluidine and *m*-toluidine see (30)]

[ $\bar{C}$  with excess  $CaBr_2$  refluxed for 40 hrs. (12) or actn. of HBr on  $\omega$ -chloroallyl aryl ethers (23) (discussed above) gives (58% yield (12)) 3-bromo-1-chloropropene-1 (const. given above); similarly  $\bar{C}$  with excess powdered  $CaI_2$  shaken at room temp. for 20 hrs. gives (65% yield (12)) (14) 1-chloro-3-iodopropene-1 (const. given above).]

[ $\bar{C}$  with NaOAc in AcOH at 110° for 16 hrs. ppts. NaCl (70% theory (12)) and gives (50% yield (12))  $\gamma$ -chloroallyl acetate [Beil. II-136], b.p. 156–159° (10), b.p. 57° at 15 mm.,  $D_4^{17} = 1.140$ ,  $n_D^{17} = 1.444$  (12).]

$\bar{C}$  reacts very slowly if at all with most metals: e.g.,  $\bar{C}$  with Zn dust in boilg. acetone or  $\bar{C}$  with Mg in dry ether (even in pres. of  $I_2$ ,  $EtBr$ , or  $HgCl_2$ ) is inert (12); however,  $\bar{C}$  with Na in tetralin (1:7550) reacts violently giving only gaseous products (12), possibly including allene (propadiene-1,2) cf. (3) (31).

[ $\bar{C}$  reacts readily with aryl MgBr cpds., with replacement of its active halogen atom by the aryl radical: e.g.,  $\bar{C}$  with  $C_6H_5MgBr$  in toluene (26) or ether (32) gives (alm. 100% yield (26))  $\gamma$ -chloroallylbenzene (1-chloro-3-phenyl-propene-1 (3:8737), b.p. 76° at 13 mm. (32),  $D_4^{25} = 1.973$  (26),  $n_D^{25} = 1.545$  (26). — For analogous reactns. of  $\bar{C}$  with *o*-tolyl-, *p*-tolyl-, *p*-cumyl-, 2-cymyl-, *p*-bromophenyl-, and *p*-methoxyphenyl-MgX cpds. see (26); for corresp. reactn. of  $\bar{C}$  with  $\alpha$ -naphthyl MgBr see (34). — For reactn. of  $\bar{C}$  with *n*-propyl MgBr see (2).]

[For reactn. of  $\bar{C}$  with diethyl sodiomalonate giving (26% yield (4)) diethyl  $\gamma$ -chloroallylmalonate, with diethyl disodiummalonate giving (32% yield (4)) diethyl bis-( $\gamma$ -chloroallyl)malonate, or with diethyl sodio-ethyl-malonate giving (20% yield (4)) diethyl  $\gamma$ -chloroallyl-ethyl-malonate see indic. refs.]

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(69) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (70) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (71) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (72) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (73) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (74) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (75) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (76) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (77) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (78) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (79) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (80) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. 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(93) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (94) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (95) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (96) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (97) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (98) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (99) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (100) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (101) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (102) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (103) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (104) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (105) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (106) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (107) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (108) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (109) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (110) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (111) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (112) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (113) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (114) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (115) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (116) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (117) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (118) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (119) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (120) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (121) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (122) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (123) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (124) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (125) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (126) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (127) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (128) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (129) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (130) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (131) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (132) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (133) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (134) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (135) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (136) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (137) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (138) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (139) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (140) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (141) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (142) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (143) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (144) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (145) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (146) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (147) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (148) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (149) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (150) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (151) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (152) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (153) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (154) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (155) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (156) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (157) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (158) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (159) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (160) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (161) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (162) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (163) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (164) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (165) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (166) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (167) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (168) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (169) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (170) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (171) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (172) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (173) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (174) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (175) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (176) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (177) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (178) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (179) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (180) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (181) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (182) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (183) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (184) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (185) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (186) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (187) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (188) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (189) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (190) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (191) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (192) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (193) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (194) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (195) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (196) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (197) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (198) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (199) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (200) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (201) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (202) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (203) Bert, Andor, *Compt. rend.* 191, 722-724 (1931); *Cent.* 1931, II 2318. (204) Bert, Andor

[ $\bar{C}$  with alcohols gives corresp. esters (for studies of rate of alcoholysis see (1) (21)); for reactn. of  $\bar{C}$  with various carbohydrates (22) and with cellulose (23) see indic. refs.;  $\bar{C}$  + phenol yields (20) phenyl dichloroacetate, m.p. 48°, h.p. 247.5° cor. (20);  $\bar{C}$  with  $\beta$ -naphthol yields (20)  $\beta$ -naphthyl dichloroacetate, m.p. 92-93° (20).]

[ $\bar{C}$  on warming with  $AlCl_3$  yields (24) (25) 1,1,1,2,2,3,3-heptachloropropane (3:0200) + chloroform (3:5050) + CO + HCl]

[ $\bar{C}$  treated with dry HI gas at -5° gives (58% yield (5)) dichloroacetyl iodide, b.p. 54-54.5° at 15 mm. (5).]

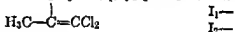
$\bar{C}$  with aq. hydrolyzes very rapidly yielding dichloroacetic acid (3:6208) q.v.; for the amide, amide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see dichloroacetic acid (3:6208).

3:5290 (1) Branch, Nixon, *J. Am. Chem. Soc.* 59, 2499-2504 (1936) (2) Otto, Beckurts, *Ber.* 14, 1618-1619 (1881). (3) Erdmann, *J. prakt. Chem.* (2) 85, 78-89 (1912). (4) Brown, *J. Am. Chem. Soc.* 60, 1325-1328 (1938). (5) Gustus, Stevens, *J. Am. Chem. Soc.* 55, 374-377 (1933). (6) Vanderstichele, *J. Chem. Soc.* 123, 1228 (1923). (7) Frankland, Patterson, *J. Chem. Soc.* 73, 187 (1898). (8) Boeseken, *Rec. trav. chim.* 29, 99-100 (1910). (9) Blaise, *Bull. soc. chim.* (4) 15, 729 (1914) (10) Carré, Liebermann, *Compt. rend.* 199, 1423 (1934).

(11) Clark, Bell, *Trans. Roy. Soc. Can.* (3) 27, III 97-103 (1933). (12) Mills (to Dow Chem. Co.), U.S. 1,921,767, Aug. 8, 1933; *Cent.* 1933, II 2595; *C.A.* 27, 5085 (1933). (13) Mills (to Dow Chem. Co.), U.S. 1,965,556, July 3, 1934, *Cent.* 1934, II 2899; *C.A.* 28, 5474 (1934). (14) Müller, Ehrmann, *Ber.* 69, 2207-2210 (1936). (15) Müller, Schumacher, *Z. physik. Chem.* B-37, 365-373 (1937). (16) Müller, Schumacher, *Z. Elektrochem.* 43, 807-808 (1937). (17) Consortium für Elektrochem. Ind., Ger. 391,674, Mar. 3, 1924, *Cent.* 1924, II 867; *Ger.* 340,872, Sept. 19, 1921; *Cent.* 1921, IV 1101; French 706,320, June 23, 1931, *Cent.* 1931, II 1489. (18) Chem. Fabrik Weiler-Meer, Ger. 362,748, Oct. 31, 1922; *Cent.* 1923, II 405. (19) McKie, *J. Chem. Soc.* 123, 2214-2215 (1923). (20) Crompton, Triffett, *J. Chem. Soc.* 119, 1874-1875 (1921).

(21) Leimu, *Ber.* 70, 1046 (1937) (22) Bell, *J. Chem. Soc.* 1935, 1180-1182. (23) Barnett, *J. Soc. Chem. Ind.* 40, T-253-256, 274 (1921) (24) Ref. 8, p. 108. (25) Böeseken, *Prins, Cent.* 1911, I 466.

3:5300 1,1-DICHLORO-2-METHYLPROPENE-1  $CH_3$   $C_4H_6Cl_2$  Beil. I-209  
( $\alpha,\alpha$ -Dichloroisobutylene)



I<sub>1</sub>—  
I<sub>2</sub>—

B.P. 108.7-109.1° (1)

108-109° (2)

107.5-108.5° (3)

$D_4^{20} = 1.449$  (3)

Note:  $\bar{C}$  by virtue of allylic transposition may yield derivatives of its synbionic isomer 1,3-dichloro-2-methylpropene-1 (3:5590) q.v.

[For prepn. of  $\bar{C}$  from  $\beta,\beta,\beta$ -trichloro-*tert*-butyl acetate (3:6180) (85% yield (3) (2)) or from  $\beta,\beta,\beta$ -trichloro-*tert*-butyl alcohol ("Chloretone") (3:2662) (very poor yield (1)) with Zn dust in alc. see (1) (2) (3); for prepn. of  $\bar{C}$  from 1,1,1-trichloro-2-bromo-2-methylpropane by htg. in quinoline (2), or from 1,1,1,2-tetrachloro-2-methylpropane (3:4725) by htg. with K in tetralin (5% yield (2)), see (2).]

$\bar{C}$  with  $Br_2$  yields (2) 1,2-dibromo-1,1-dichloro-2-methylpropane, m.p. 209° (s.t.) (2).

3:5300 (1) Bruyne, Davis, Cross, *Physik. Z.* 33, 720 (1932). (2) Jacob, *Bull. soc. chim.* (5) 7, 581-586 (1940); *C.A.* 36, 3507 (1942). (3) Favorskii, Jozitsch, *Cent.* 1899, I 778. (4) Jozitsch, *Cent.* 1899, I 606.

3:5330 1,1,2-TRICHLOROETHANE  
(*unsym.*-Trichloroethane,  
chloroethylidene (di)chloride)

 $\text{C}_2\text{H}_3\text{Cl}_3$ 

Boil: I - 85  
I<sub>1</sub>-(24)  
I<sub>2</sub>-(55)

B.P.

F.P.

113.2° at 767.7 mm. (1)	-37.4° (8)	$D_4^{25} = 1.4315$ (13)	$n_D^{25} = 1.47345$ (7)
114° at 767 mm. (13)	-39.0° (11)		
114° at 760 mm. (2)	-35.5° (5)	$D_4^{20} = 1.443$ (2)	$n_D^{20} = 1.4708$ (12)
113.72° at 760 mm. (3)		1.4416 (13)	1.47064 (8)
113.65° at 760 mm. (4)		1.4411 (8)	
113.5° at 760 mm. (6) (6)			
113.5° (7)			
113.3° cor. at 760 mm. (8)			
113.2° (9)			
112.5-113° (10)			

Care must be taken to avoid confusion of  $\bar{\text{C}}$  with the isomeric 1,1,1-trichloroethane (3:5085).  $\bar{\text{C}}$  is now comm. prod. in U.S. (14).

### MISCELLANEOUS PHYSICAL PROPERTIES

sol. nq.; e.g., 100 g. aq. at 0° dis. 0.460 g.  $\bar{\text{C}}$  (15). — [For soly. of aq. in  $\bar{\text{C}}$  at 0°, (16).]  
d press. see (10).]

[For soly. of  $\text{I}_2$  in  $\bar{\text{C}}$  see (17).]

Binary systems contg.  $\bar{\text{C}}$ . (See also below under uses of  $\bar{\text{C}}$ .)  $\bar{\text{C}}$  + 1,2-dichloroethane (ethylene dichloride) (3:5130): for t.p./compn. datn, eutectic f.p. -70° (11), and for  $D$  and vapor/liq. equil. (13), see indic. refs.

Azeotropes contg.  $\bar{\text{C}}$ .  $\bar{\text{C}}$  with  $\text{EtOH}$  (1:6130) forms a const.-boilg. mixt., b.p. 77.8° (4), 77.3° (6) at 760 mm., contg. 35 (6), 30 (1) wt. %  $\bar{\text{C}}$ .

Other physical props. [For study of thermal conductivity of  $\bar{\text{C}}$  see (18).]

### USES OF $\bar{\text{C}}$

$\bar{\text{C}}$  is now widely used as industrial solvent and in other ways [e.g., for use of  $\bar{\text{C}}$  (10%) 1,1,1-trichloroethane (3:5085) + 20% pet. hydrocarbons as dry-cleaners' solv. see (10); for use of  $\bar{\text{C}}$  + ethylene dichloride (3:5130) as hair wash see (20); for use of  $\bar{\text{C}}$  + *n*-heptane (1:8575),  $\bar{\text{C}}$  + cyclohexane (1:8105), or  $\bar{\text{C}}$  +  $\text{C}_6\text{H}_6$  (1:7400) as test mixts. for detn. of number of theoret. pl. in fractionating columns see (21); for use of  $\bar{\text{C}}$  in dewaxing of oils see (22)].

### PHYSIOLOGICAL ACTION AND TOXICITY

Full treatment of this topic is beyond the scope of this work [however, for lead references see (23) (24) (25) (26) (27) (27)]. — For study of  $\bar{\text{C}}$  as anthelmintic see (28)].

### PREPARATION OF $\bar{\text{C}}$

From vinyl chloride (3:7010). (See also below under acetylene.) [For prepn. of  $\bar{\text{C}}$  from vinyl chloride with  $\text{Cl}_2$  at 0-80° in light or at 180-250° in absence of light or solv. see (29) (30) (31) cf. (32); for study of photochemical addn. of  $\text{Cl}_2$  to vinyl chloride yielding  $\bar{\text{C}}$  see (33).]

From 1,2-dichloroethylene (3:5030). [For prepn. of  $\bar{\text{C}}$  from 1,2-dichloroethylene by addn. of  $\text{HCl}$  gas at 30-40° in pres. of  $\text{AlCl}_3$  (85% yield) see (34) (37) (note that 1,1,2,3,4-pentachlorobutane (3:0750) is also obtd. as a by-product (36)).]

From 1,1-dichloroethane (ethylidene (di)chloride) (3:5035). [For formn. of  $\bar{C}$  from ethylidene (di)chloride with  $SbCl_5$  (3 wt. parts) on refluxing see (36).]

From 1,2-dichloroethane (ethylene (di)chloride) (3:5130). [For prepn. of  $\bar{C}$  from ethylene (di)chloride with  $Cl_2$  in ultra-violet light at  $50^\circ$  (38) (39) or  $25^\circ$  (40), or with  $Cl_2$  + suitable cat. at not above  $60^\circ$  (41), or  $\bar{C}$  (as liquid) with  $Cl_2$  (7), or with  $Cl_2$  in pres. of  $AlCl_3/NaCl/FeCl_3$  at  $300-425^\circ$  as directed (42), or with  $SO_2Cl_2$  + trace dibenzoyl peroxide refluxed 2 hrs in dark (12) (yields: 80% (41), 70% (40) (12), 50% (42)), see indic. refs.]

From ethylene. [For prepn. or formn. of  $\bar{C}$  from ethylene with  $Cl_2$  + cat. see (43) (44) (45) (46) (47).]

From acetylene. [For prepn. of  $\bar{C}$  from acetylene with  $HCl$  +  $Cl_2$  + cat. (doubtless via formn. of vinyl chloride (and subsequent addn. of  $Cl_2$  as above) see (48) (30).]

From other sources. [For formn. of  $\bar{C}$  as by-prod. of prepn. of chloral (3:5210) see (49); for prepn. of  $\bar{C}$  from 2,2-dichloroethanol-1 (3:5745) with  $PCl_5$  (50), or from  $\alpha,\beta$ -dichloroethyl chloroformate by loss of  $CO$  under influence of  $AlCl_3$  (51), see indic. refs.; for formn. of  $\bar{C}$  from trichloroethylene (3:5170) with  $Hl$  for 2 weeks in sunlight see (68).]

## CHEMICAL BEHAVIOR OF $\bar{C}$

Dehydrochlorination.  $\bar{C}$  under suitable conditions may lose  $HCl$  in either or both of two modes yielding either or both 1,1-dichloroethylene (vinylidene (di)chloride) (3:5005) or a mixt. of the stereoisomeric 1,2-dichloroethylenes (3:5030). — [E.g.,  $\bar{C}$  with alc.  $KOH$  (52) (53) (54), or with excess aq.  $Ca(OH)_2$  at  $70-80^\circ$  (55) (56), or with aq. or alc.  $NH_3$  (57), or even with  $Na$  in ether (58) gives (yields 100% (57), 90% (55) (56)) 1,1-dichloroethylene (3:5005). — On the other hand,  $\bar{C}$  pyrolyzed at  $400^\circ$  over pumice contg.  $CuCl_2$  (59) is claimed to give mainly 1,2-dichloroethylene (3:5030). — Note also that  $\bar{C}$  with  $MeOH$  over  $Al_2O_3$  at  $290^\circ$  gives (60) a mixt. of both prods. together with  $MeCl$  (3:7905).]

[Note in this connection that  $\bar{C}$  with aq. +  $Zn$ ,  $Fe$ , or  $Al$  at  $100-120^\circ$  under press. yields (61) vinyl chloride (3:7010); perhaps this occurs by way of the above dichloroethylenes as intermediate.]

Halogenation of  $\bar{C}$ . Chlorination. ( $\bar{C}$  with  $Cl_2$  +  $AlCl_3$  at  $70-80^\circ$  yields (62) 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750).]

Fluorination. ( $\bar{C}$  with  $HgF_2$  under press. at  $140^\circ$  gives (63) 50% 1,2-dichloro-1-fluoroethane + 10% 2-chloro-1,1-difluoroethane; for behavior of  $\bar{C}$  with  $SbF_3$  +  $Br_2$  at  $160^\circ$ , with  $SbF_3$  +  $SbCl_5$ , or with  $SbF_3Cl_2$  see (63).]

Behavior of  $\bar{C}$  with other inorganic reactants. ( $\bar{C}$  with alkali hydroxide on fusion at  $250-300^\circ$  yields (64) salts of glycolic acid (1:0430).]

Behavior of  $\bar{C}$  with organic reactants. ( $\bar{C}$  with 1,2-dichloroethylene (3:5030) + 1%  $AlCl_3$  at  $35-40^\circ$  for 5 days yields (37) a mixt. of two stereoisomeric 1,1,2,3,4-pentachlorobutanes, viz. the liq. isomer (3:9068) and the solid isomer (3:0750). —  $\bar{C}$  + trichloroethylene (3:5170) + 1-2%  $AlCl_3$  at  $40^\circ$  for 7 days yields (37) 1,1,1,4,4-pentachlorobutene-2 (3:9054).]

( $\bar{C}$  with  $C_6H_6$  +  $AlCl_3$  gives (31% yield (65)) 1,1,2-triphenylethane, b.p.  $211^\circ$  at 14 mm., accompanied by diphenylmethane and 1,2-diphenylethylene (stilbene).]

( $\bar{C}$  with  $C_6H_5MgBr$  in toluene does not react even at  $100^\circ$  (66).]

Comment on Fujiwara reaction.  $\bar{C}$  does not respond to Fujiwara reactn. (pyridine +  $NaOH$ ) (23).

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(11) Timmermans, Veselovsky, *Bull. soc. chim. Belg.* 40, 505 (1931). (12) Kharasch, Brown, *J. Am. Chem. Soc.* 61, 2145 (1939). (13) Portnov, Seferovich, *Trans. State Inst. Applied Chem. (U.S.S.R.)* 21, 81-89 (1935); not in *Cent.*; C.A. 29, 7272 (1935). (14) McLure, *Chem. Eng. News* 22, 421 (1944). (15) van Arkel, Vles, *Rec. trav. chim.* 55, 410 (1936). (16) Staverman, *Rec. trav. chim.* 60, 836-841 (1941); *Cent.* 1942, I 1352; C.A. 37, 2638 (1943). (17) Margosches, Hinner, Friedmann, *Z. anorg. allgem. Chem.* 137, 87-99 (1921). (18) Bates, Hazard, Palmer, *Ind. Eng. Chem.* 33, 375-376 (1941). (19) Parkhurst (to Standard Oil of California), U.S. 1,948,045, Feb. 20, 1931; *Cent.* 1931, II 563; C.A. 23, 2924 (1931). (20) Cathala, *French* 598,518, Dec. 18, 1925; *Cent.* 1926, I 2752, not in C.A.

(21) Stage, Schultze, *Oel u. Kohle* 40, 90-95 (1944); C.A. 38, 6131 (1944). (22) Sharples Specialty Co., *French* 691,583, Aug. 7, 1936; *Cent.* 1937, I 263; C.A. 31, 535 (1937). (23) Barrett, Cunningham, Johnston, *J. Ind. Hyg. Toxicol.* 21, 470-480 (1939). (24) von Oettingen, *J. Ind. Hyg. Toxicol.* 19, 395-399 (1937). (25) Schmander, *Arch. Gewerbepathol. Gewerbhyg.* 7, 109-116 (1939); *Cent.* 1939, II 1331; not in C.A. (26) Barsoun, Sand, Quart, *J. Pharm. Pharmacol.* 7, 295-214 (1931); *Cent.* 1931, II 2550; C.A. 23, 6194 (1931). (27) Lazarev, *Arch. exptl. Path. Pharmacol.* 141, 19-21 (1929); *Cent.* 1929, II 451; C.A. 23, 3074 (1931). (28) Wright, Schaffer, *Am. J. Hyg.* 16, 372-374 (1932). (29) Ernst, Lango (to I.G.), U.S. 1,833,355, 1,833,393, Nov. 24, 1931; C.A. 26, 1301 (1932); *Ger.* 459,454, Jan. 17, 1930; (*Cent.* 1930, I 3829; C.A. 24, 2145 (1930)); *Brit.* 295,681, Nov. 28, 1928; *Cent.* 1929, I 1396; C.A. 23, 2721 (1929). (30) I.G., *French* 690,655, Sept. 21, 1930; *Cent.* 1931, I 1164; C.A. 23, 1261 (1931); *Brit.* 319,097, March 11, 1929; C.A. 26, 6314 (1932); not in *Cent.*

(31) Consortium für Elektrochem. Ind., *French* 690,707, Sept. 25, 1930; *Cent.* 1931, I 1164; C.A. 23, 1261 (1931). (32) Bilts, *Ber.* 35, 3526-3527 (1902). (33) Schmitz, Schumacher, *Z. physik. Chem. B-52*, 73-80 (1942). (34) Prins, *Rec. trav. chim.* 45, 80-81 (1926). (35) Müller, Hdon, *J. prakt. Chem.* (2) 133, 289-290 (1932). (36) Meyer, Müller, *J. prakt. Chem.* (2) 46, 174-175 (1902). (37) Prins, *Rec. trav. chim.* 56, 119-125 (1937). (38) Coleman, Moore (to Dow Chem. Co.), U.S. 2,174,737, Oct. 3, 1939; C.A. 31, 779 (1940). (39) Compagnie des Prod. Chim. d'Alsai, etc., *French* 604,491, Oct. 21, 1930; *Cent.* 1937, I 1545; C.A. 31, 3500 (1937). (40) Maler, *Ger.* 522,950, April 20, 1931; (*Cent.* 1931, I 13607; C.A. 25, 3679 (1931); *French* 655,930, April 25, 1929; *Cent.* 1929, II 1347; C.A. 23, 3931 (1929)).

(41) Jung, Zimmermann, *Ger.* 545,993, March 8, 1932; *Cent.* 1932, I 2803; C.A. 26, 3520 (1932). (42) Reilly (to Dow Chem. Co.), U.S. 2,149,549, Dec. 20, 1938; *Cent.* 1939, I 3025; C.A. 23, 2510 (1939). (43) Gavet, *Ber.* 76, 1115-1118 (1943); C.A. 38, 4901 (1944). (44) Golov, *Sbornik Diklorotan* 1939, 18-20; C.A. 36, 2523 (1942). (45) Bahr, Zieler, *Z. anorg. Chem.* 43, 233-236 (1930). (46) Stewart, Smith, *J. Am. Chem. Soc.* 51, 3032-3095 (1929). (47) Askenasy, Heller, *Ger.* 549,841, April 26, 1932; *Cent.* 1932, II 286; C.A. 26, 3507 (1932). (48) I.G., *French* 687,397, Aug. 7, 1930; *Cent.* 1930, II 3637; C.A. 23, 715 (1931); *Brit.* 344,592, Jan. 31, 1929; C.A. 26, 155 (1932); not in *Cent.* (49) Kraemer, *Ber.* 3, 261 (1870). (50) Delcure, *Compt. rend.* 104, 1156 (1887).

(51) Müller, *Ann.* 238, 58 (1890). (52) Brockway, Beach, Pauling, *J. Am. Chem. Soc.* 57, 2695 (1935). (53) Regnault, *J. prakt. Chem.* (1) 18, 82-85 (1839); *Ann. chim.* (2) 69, 155-159 (1835). (54) Kilmont, *Chem. Ztg.* 46, 521 (1922). (55) I.G., *Brit.* 319,872, July 2, 1931; *Cent.* 1931, II 1191; C.A. 26, 5314 (1932); *French* 702,361, April 7, 1931; *Cent.* 1931, II 1191; C.A. 25, 4285 (1931); *Ger.* 529,604, July 4, 1929; C.A. 23, 5178 (1931); not in *Cent.* (56) Howell (to Imp. Chem. Ind., Ltd.), *Brit.* 531,733, March 17, 1941; C.A. 36, 1336 (1942). (57) Engel, *Bull. soc. chim.* (2) 48, 97 (1887). (58) Brunner, Brandenburg, *Ber.* 10, 1497-1499 (1877); 11, 61-62 (1878). (59) Hermann, Baum (to Consortium für Elektrochem. Ind.), U.S. 1,921,679, Aug. 8, 1933; C.A. 27, 5086 (1933); not in *Cent.*; *Ger.* 570,954, Feb. 22, 1933; C.A. 27, 4253 (1933); not in *Cent.*; *French* 694,054, Nov. 28, 1930; *Cent.* 1931, I 1514; C.A. 25, 1843 (1931). (60) I.G., *French* 803,563, Nov. 21, 1930; *Cent.* 1937, I 2258; C.A. 31, 4345 (1937).

(61) I.G., *Ger.* 525,300, May 21, 1931; *Cent.* 1931, II 1055; C.A. 25, 4012 (1931); *French* 703,767, May 6, 1931; *Cent.* 1931, II 1053; C.A. 25, 4557 (1931). (62) Taurikh, *Trans. State Inst. Applied Chem. (U.S.S.R.)* 24, 77-80 (1935); C.A. 29, 7272 (1935); not in *Cent.* (63) Henne, Renoll, *J. Am. Chem. Soc.* 58, 889-890 (1936). (64) Strossacker, Pelton (to Dow Chem. Co.), U.S. 1,881,354, Oct. 25, 1932; *Cent.* 1933, I 367; C.A. 27, 1006 (1933). (65) Bert, *Compt. rend.* 213, 792-793 (1941); *Cent.* 1942, II 1785; C.A. 37, 4965 (1943). (66) Bert, *Bull. soc. chim.* (4) 41, 1173 (1927). (67) Lehman, Schmidt-Kehl, *Arch. Hyg. Bakt.* 116, 131-268 (1936); C.A. 31, 477 (1937); not in C.A. (68) Kharasch, Norton, Mayo, *J. Org. Chem.* 3, 40-50 (1935).

3:5345 3,3,3-TRICHLOROPROPENE-1  $\text{Cl}_3\text{C}-\text{CH}=\text{CH}_2$   $\text{C}_3\text{H}_2\text{Cl}_3$  Beil. I-200  
(1,1,1-Trichloropropene-2)  $\text{I}_1-$   
 $\text{I}_2-$

B.P.	M.P.		
114-115° at 760 mm. (1)	-30° (2)	$D_{20}^{20} = 1.369$ (1)	$n_D^{20} = 1.4827$ (3)
114-115° at 757 mm. (2)	-55- -50° (1) (5)		(5)
57° at 103 mm. (3)		$D_{13}^{13} = 1.359$ (2)	

Liquid with penetrating odor suggesting aldehydes. [For use in dewaxing of mineral oil see (4).]

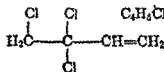
[For prepn. of  $\bar{\text{C}}$  from 1,1,1-trichloropropanol-2 (3:0846) (84% yield (3)) with  $\text{P}_2\text{O}_5$  (3) (2) (1), with  $\text{PCl}_3$  (5) (1), or with  $\text{PCl}_5$  (5) (1) see indic. refs.]

$\bar{\text{C}}$  in cold and in diffused light adds  $\text{Cl}_2$  yielding (2) 1,1,1,2,3-pentachloropropane (3:4740), m.p. 179-180° (2). —  $\bar{\text{C}}$  adds  $\text{Br}_2$  readily yielding (2) 1,1,1-trichloro-2,3-dibromopropane [Beil. I-112], cryst. from alc., m.p. 210° (2)

$\bar{\text{C}}$  with  $\text{HCl} + \text{FeCl}_3$  at 50° for 50-100 hrs. gives (20% yield (3)) 1,1,1,2-tetrachloropropane (3:5785). — [For study of addn. to  $\bar{\text{C}}$  of  $\text{HBr}$  see (3).]

3:5345 (1) Henry, *Bull. acad. roy. Belg.* 1905, 101-121; *Cent.* 1905, I 1697. (2) Victoria, *Rec. trav. chim.* 24, 280-283 (1905). (3) Kharasch, Rossin, Fields, *J. Am. Chem. Soc.* 63, 2558-2560 (1941) (4) Standard Oil Development Co., French 790,852, Nov. 23, 1935, *Cent.* 1936, I 2672, *C.A.* 30, 3223 (1936). (5) Henry, *Rec. trav. chim.* 24, 336-344 (1905).

3:5350 3,4-DICHLOROBUTENE-1  $\text{C}_4\text{H}_2\text{Cl}_2$  Beil. S.N. 12  
(1,2-Dichlorobutene-3)



B.P. 115° (1)	$n_D^{20} = 1.4550$ (1)
45-45.5° at 40 mm. (1)	

[For prepn. of  $\bar{\text{C}}$  (together with other products) from butadiene-1,3 with  $\text{Cl}_2$ , either directly or in  $\text{CHCl}_3$ ,  $\text{CS}_2$  or lgr. soln., see (1) (2), the process can be controlled so as to yield little or no 1,2,3,4-tetrachlorobutane but rather a mixt. of  $\bar{\text{C}}$  and 1,4-dichlorobutene-2 (3:5725) in the ratio 2:1 (1) (2).]

$\bar{\text{C}}$  does not (1) rearr. to 1,4-dichlorobutene-2 (3:5725) even on htg at 90° in a s.t. — However,  $\bar{\text{C}}$  in the presence of a metal halide cat. (3) such as  $\text{AlCl}_3$  (4) rearr. by allylic transposition to 1,4-dichlorobutene-2.

$\bar{\text{C}}$  on htg. at 90° with 2 pts. solid  $\text{KOH}$  loses  $\text{HCl}$  yielding (1) (2) 1-chlorobutadiene-1,3 (3:7210), b.p. 85° (1) (2); under certain conditions, however,  $\bar{\text{C}}$  with  $\text{KOH}$  loses  $\text{HCl}$  to yield (5) 2-chlorobutadiene-1,3 (chloroprene) (3:7080).

$\bar{\text{C}}$  on htg. in alc. with  $\text{Zn}$  dust yields (1) butadiene-1,3.

$\bar{\text{C}}$  with  $\text{Cl}_2$  yields solely (1) the liq. isomer of 1,2,3,4-tetrachlorobutane (3:6082).

$\bar{\text{C}}$  treated directly with  $\text{O}_2$  at 0°, then with aq., yields (1)  $\alpha,\beta$ -dichloropropionaldehyde (3:9034), b.p. 73° at 50 mm. (1), + formaldehyde (1:0145). —  $\bar{\text{C}}$  on oxidn. with dil. alc.  $\text{KMnO}_4$  gives (1)  $\alpha,\beta$ -dichloropropionic acid (3:0555), m.p. 50° (1).

3:5350 (1) Muskat, Northrup, *J. Am. Chem. Soc.* 63, 4043-4055 (1930). (2) Muskat (to du Pont), U.S. 2,038,593, Apr. 28, 1936; *Cent.* 1936, II 3358; *C.A.* 30, 3912 (1936). (3) I.G. Farbenindustrie, Brit. 505,573, May 12, 1939, *Cent.* 1939, II 1572, *C.A.* 33, 7822 (1939). (4) Nicodemus (to I.G.), U.S. 2,242,054, May 13, 1941; *C.A.* 35, 5131 (1941). (5) Carothers (to du Pont), U.S. 2,038,538, Apr. 25, 1936; *Cent.* 1936, II 3358; *C.A.* 30, 3838 (1936).



3:5356 CHLOROMETHYL ACETATE  $\text{CH}_3\text{CO.O.CH}_2\text{Cl}$   $\text{C}_3\text{H}_5\text{O}_2\text{Cl}$  Beil. II - 152 $\text{II}_1$ — $\text{II}_2$ -(160)

B.P. 115–116° at 757 mm. (1)

 $D_{15}^{20} = 1.1953$  (1) (13)

115° at 757 mm. (13)

115° (5)

113–115° (2) (12)

110–112° (3)

68–62° at 290 mm. (4)

Colorless liq. with penetrating odor. — Insol. cold aq.; sol. alc., ether. — Sol. in cold conc.  $\text{H}_2\text{SO}_4$  with evoln. of  $\text{HCl}$  (1) (13).

[For prepn. of  $\bar{\text{C}}$  from methyl acetate (1:3005) with  $\text{Cl}_2$  in cold (1) (5) and in sunlight (2) (6), or with  $\text{SO}_2\text{Cl}_2$  in sunlight (6), see indic. refs.; from polyoxymethylene with  $\text{AcCl}$  (3:7065) in s.t. at 100° (6) or by htg. in pres. of  $\text{ZnCl}_2$  (61% yield on  $\text{AcCl}$  (4)) cf. (7) (8) (note that crude  $\bar{\text{C}}$  may be more or less contaminated with bis-(chloromethyl ether) (3:5245), b.p. 105°, and  $\text{Ac}_2\text{O}$  (1:1015), b.p. 140°, apparently produced by disproportionation of  $\bar{\text{C}}$  itself during the htg. (7).]

$\bar{\text{C}}$  on slight warming with aq. readily dissolves by virtue of hydrolysis, yielding (1) (5) (3) formaldehyde (1:0145),  $\text{AcOH}$  (1:1010), and  $\text{HCl}$ .

[ $\bar{\text{C}}$  with alcs. or Na alcoholates (10) presumably first yields alkoxyethylacetates: e.g.,  $\bar{\text{C}}$  with Na benzylate in  $\text{C}_6\text{H}_6$  refluxed for 4 hrs. gives (15% yield (4)) benzyloxyethyl acetate, b.p. 152–155° at 29 mm. (4); however, the usual type of prod. consists of a mixture of formaldehyde dialkylacetal and alkyl acetate (perhaps formed by interchange of radicals between the initial product and the alcohol (9)): e.g.,  $\bar{\text{C}}$  with benzyl alc. (1:6480) gives (9) (10) (13) formaldehyde dibenzylacetal, b.p. 188–190° at 13 mm., + benzyl acetate (1:3751), b.p. 217°;  $\bar{\text{C}}$  with *n*-propyl alc. (1:6150) gives (9) (13) formaldehyde di-*n*-propylacetal [Beil. I-575, I<sub>1</sub>-(301), I<sub>2</sub>-(639)], b.p. 137° at 760 mm., + *n*-propyl acetate (1:3075), b.p. 101.6°; for analogous behavior of  $\bar{\text{C}}$  with  $\text{MeOH}$  (1:6120) and  $\text{EtOH}$  (1:6130) see (10).]

[ $\bar{\text{C}}$  with Na phenolate does not yield phenoxymethyl acetate but instead (45% yield (11)) phenyl acetate (1:3571); this may be accounted for in a fashion completely analogous to that suggested above in the case of alcs., but no attempt was made (11) to verify the pres. of formaldehyde diphenylacetal (diphenoxymethane) although the latter [Beil. VI-150] is well known.]

$\bar{\text{C}}$  with  $\text{NH}_3$  in dry ether gives (12) (13) acetamide,  $\text{NH}_4\text{Cl}$  + formaldehyde (often in the form of hexamethylenetetramine (13)). —  $\bar{\text{C}}$  with aniline (1.5 moles) in dry ether gives (80% yield (12)) acetanilide, m.p. 114–115°, + 1,3,5-triphenyltrimethylenetriamine ("anhydroformaldehydeaniline") [Beil. XXVI-3], yel. pr., m.p. 140–141° (produced by actn. of the liberated formaldehyde upon the excess of aniline). — [ $\bar{\text{C}}$  (1 mole) with *N,N*-dimethylaniline (2 moles) +  $\text{ZnCl}_2$  at 110–120° gives (5) salt of 4,4'-bis-(dimethylamino)-diphenylmethane [Beil. XIII-239, XIII<sub>1</sub>-(71)], m.p. 91°.]

$\bar{\text{C}}$  with pyridine forms an unstable addn. cpd. (12);  $\bar{\text{C}}$  with quinoline forms (12) an addn. cpd., m.p. 214–216° dec., eas. sol. in abs. alc. but easily pptd. with dry ether (12).

[ $\bar{\text{C}}$  with *N*-potassio pyrrole in dry ether gives (18% yield (14)) *N*-pyrrylmethyl acetate, b.p. 59–63.5° at 3 mm.,  $D_4^{20} = 1.0916$ ,  $n_D^{20} = 1.4907$  (14).]

[For study of rate of reactn. of  $\bar{\text{C}}$  with  $\text{KI}$  in acetone at 20° and 25° see (2).]

3:5356 (1) Henry, *Ber.* 6, 740–741 (1873). (2) Conant, Kirner, Hussey, *J. Am. Chem. Soc.* 47, 497, 499 (1925). (3) Descude, *Compt. rend.* 132, 1568 (1901). (4) Gupta, Kaushal, Deshpande, *J. Indian Chem. Soc.* 18, 638–640 (1911). (5) Censi, *Bull. soc. ind. Mulhouse* 70, 311–

313 (1899); *Cent.* 1900, I 594-595. (6) Henry, *Bull. acad. roy. Belg.* 1900, 48-50, *Cent.* 1900, I 1122-1123. (7) Descude, *Bull. soc. chim.* (3) 27, 807-809 (1902); *Compt. rend.* 132, 1503 (1901). (8) Henry, *Compt. rend.* 133, 97 (1901). (9) Descude, *Bull. soc. chim.* (3) 27, 47-48 (1903). (10) Descude, *Bull. soc. chim.* (3) 27, 1215-1219 (1902). (11) Kirner, *J. Am. Chem. Soc.* 48, 2748 (1926). (12) Ulich, Adams, *J. Am. Chem. Soc.* 43, 663, 665-666 (1921). (13) Descude, *Ann. chim.* (7) 29, 504-508 (1903). (14) Taggart, Richter, *J. Am. Chem. Soc.* 56, 1356 (1934).

3:5358 3-CHLORO-1,2-EPOXYPROPANE  
 ("Epichlorohydrin";  
 $\gamma$ -chloropropylene oxide;  
 (chloromethyl)ethylene oxide)

C<sub>3</sub>H<sub>5</sub>OClBeil. XVII - 6  
XVII-(4)

B.P.		M.P.	
(118-119°)	(1) (50)	-48°	(10) $D_4^{25} = 1.17495$ (23)
117°	(2) (3) (4) (5)		1.1723 (24)
116.5-117.5°	at 765 mm. (6)		$n_D^{25} = 1.43585$ (23)
116.75-117.00°	at 762.2 mm. (7)		$D_4^{20} = 1.184$ (26)
116.50°	at 760 mm. (7)		1.1812 (10)
116.5°	at 761 mm. (8)		1.181 (17)
116.45°	at 760 mm. (9)		1.1801 (25)
117°	at 758 mm. (10)		1.18 (18)
117° cor.	at 765 mm. (11)		$n_D^{20} = 1.4382$ (26)
116-118°	(12)		1.438 (17)
116-117°	at 760 mm. (13)		$D_4^{18.1} = 1.1848$ (25)
116°	(14) (15)		$n_D^{16.1} = 1.43000$ (25)
115-117°	(16)		$D_4^{11.5} = 1.1928$ (26)
115-116°	(17) (18) (48)		$n_D^{11.5} = 1.44105$ (26)
115.4°	at 764 mm. (19)		
115° cor.	at 740 mm. (20)		
	(21)		
60-61°	at 100 mm. (17)		
30-32°	at 10 mm. (22)		

$\tilde{C}$  is also sometimes designated as " $\alpha$ -epichlorohydrin" to distinguish it from the less common " $\beta$ -epichlorohydrin" =  $\beta$ -chlorotrimethylene oxide.

$\tilde{C}$  is liq. with odor suggesting chloroform. —  $\tilde{C}$  is spar. sol. aq. (see also below) but misc. with alc. or ether.

### MISCELLANEOUS PHYSICAL PROPERTIES

Solubility relations.  $\tilde{C}$  with aq. forms two layers: the lower layer conts. the following no. of g.'s  $\tilde{C}$  per 100 g. satd. soln.: at 25° 98.48 g., at 45° 97.43 g., at 70° 95.82 g., at 80.4° 94.17 g.; the upper layer conts. per 100 g. satd. soln.: at 30.2° 6.60 g., at 52.0° 7.53 g., at 65.0° 8.45 g., at 72.0° 9.34 g., at 80.2° 10.43 g. (5).

Binary azeotropes contg.  $\tilde{C}$ .  $\tilde{C}$  with aq. forms a homogeneous const. boilg. mixt., b.p. 88°, contg. 75%  $\tilde{C}$ ; at 25° this azeotrope seps. into two layers contg. respectively 98%  $\tilde{C}$  and 7%  $\tilde{C}$  (17).

[ $\tilde{C}$  with AcOH (1:1010) forms (9a) a const.-boilg. mixt., b.p. 115.05° at 760 mm., contg. 65.5 wt. %  $\tilde{C}$ ;  $\tilde{C}$  with tetrachloroethylene (3:5460) forms (9b) a const.-boilg. mixt., b.p. 110.12° at 760 mm., contg. 51.5 wt. %  $\tilde{C}$ .]

[Note that  $\bar{C}$  with EtOH (1:6130) (9c) or with formic acid (1:1005) (9d) forms no azeotropes.]

Ternary systems contg.  $\bar{C}$ . [For extensive study of system  $\bar{C}$  + AcOH + aq. see (5).]

### MISCELLANEOUS PHYSIOLOGICAL AND BIOCHEMICAL BEHAVIOR OF $\bar{C}$

[For study of toxicity of  $\bar{C}$  see (27); for effect on proteins see (28); for effect on wire worms see (29).]

### USES OF $\bar{C}$

The uses of  $\bar{C}$  both as solvent and as chemical intermediate (see below) are manifold and cannot here be reviewed in detail [however, for use of  $\bar{C}$  in stabilization of nitrate esters (30), in refining of mineral oil (31), or in treatment of cellulose fibers to improve dyeing with acid dyes (32) see indic. refs.].

### PREPARATION OF $\bar{C}$

[For prepn. of  $\bar{C}$  from 1,3-dichloropropanol-2 ("α-dichlorohydrin") (3:5935) with aq. Ca(OH)<sub>2</sub> (22) (16) (33), with aq. NaOH (4) (13) (17) (34) (37) cf. (35), with alc. NaOH (36), with ether + NaOH (38), with solid NaOH (39), or with aq. KOH (2) (1) (yields: 95% (33), 92.5% (36), 90% (13) (16) (34), 85% (17), 79% (2), 76-81% (38), 67-72% (22), 70% (17), 60% (4)) see indic. refs.; for patents on prepn. of  $\bar{C}$  from this source by use of various alk. materials see (40) (41) (33) (37); note that during this type of prepn. of  $\bar{C}$  some glycerol (1:6540) is also formed (38) (44).]

[For prepn. of  $\bar{C}$  from 2,3-dichloropropanol-1 ("β-dichlorohydrin") (3:6060) with aq. alk. see (42) (for studies of kinetics of this loss of HCl see (43)).]

[For formn. of  $\bar{C}$  from glycerol (1:6540) with PCl<sub>3</sub> (45), with HCl (1) (50), or S<sub>2</sub>Cl<sub>2</sub> (50) see indic. refs.]

[For formn. of  $\bar{C}$  from sodium salt of γ-chloro-β-hydroxy-*n*-propyl hydrogen sulfite (itself obtd. from  $\bar{C}$  + NaHSO<sub>3</sub>) on treatment with NaOH see (46).]

[For formn. of  $\bar{C}$  from 1-bromo-3-chloropropanol-2 (see below) by loss of HBr by actn. of conc. KOH see (1).]

### CHEMICAL BEHAVIOR OF $\bar{C}$ WITH INORGANIC REACTANTS

Reduction of  $\bar{C}$ . [ $\bar{C}$  with Na/Hg in moist ether is very slowly attacked and some allyl alc. (1:6145) (together with other prods.) is formed (47). — Note, however, that reactn. of  $\bar{C}$  with Nn in ether is very complicated and the prods. and mode of their formn. are disputed (48) (49) (44) (50) (51).] — (For behavior of  $\bar{C}$  with H<sub>2</sub> see below.)

Oxidation of  $\bar{C}$ . [ $\bar{C}$  on oxidn. with HNO<sub>3</sub> (*D* = 1.38) gives (52) β-chloro-α-hydroxypropionic acid (β-chlorolactic acid) [Beil. III-286, III<sub>1</sub>-(110), III<sub>2</sub>-(209)], cas. sol. aq., alc., ether, cryst. from C<sub>6</sub>H<sub>6</sub> (53), m.p. 77° (53), 77-78° (52) (for resolution of this prod. into opt. act. forms, *d*-form, m.p. 91.5°, see (54)). — Note that this prod. is also obtd. by oxidn. of 3-chloropropanediol-1,2 ("α-monochlorohydrin") (3:9038) q.v.]

Halogenation of  $\bar{C}$ . [ $\bar{C}$  with Cl<sub>2</sub> in diffuse light gives (55) γ,γ-dichloropropylene oxide [Beil. XVII-9], oil, b.p. 170°. —  $\bar{C}$  with Br<sub>2</sub> at 100° gives (56) (57) *x,x,x*-tribromo-γ-chloropropylene oxide [Beil. XVII-9], oil, which on shaking with aq. forms a crystn. tetrahydrate, m.p. 55° (56).]

Behavior of  $\bar{C}$  with water (or dil. acids). [ $\bar{C}$  with aq. at 100° (6) in s.t. (1) cf. (60) or on boilg. for 14 hrs. (58) adds H<sub>2</sub>O giving (80% yield (58)) 3-chloropropanediol-1,2 (α-

monochlorohydrin) (3:9038). This process is greatly facilitated by the pres. of dil. acids: e.g., for use of dil.  $H_2SO_4$  (yields: 85-90% (34) cf. (59), 80% (36)) or formic acid (66% yield (212)) see indic. refs.; for study of kinetics of this reactn. incl. influence of various acids and salts see (6) (19) (61) (62); for patent on use of dil. acids or acid-reacting salts see (63). — Note, however, that  $\bar{C}$  with aq. contg. 3-20%  $H_2SO_4$  at 100-250° under press. gives (72) acrolein (1:0115).]

Behavior of  $\bar{C}$  with halogen hydrides (HX). With HF. [ $\bar{C}$  with 30% HF soln. reacts vigorously yielding (64a) 3-chloropropanediol-1,2 ("α-monochlorohydrin") (3:9038) and other prods; note that  $\bar{C}$  with HIF under some circumstances appears to yield (64b) polymers.]

With HCl. [ $\bar{C}$  with conc. HCl shaken several hrs. at room temp. (3) (4) cf. (19) (65), or  $\bar{C}$  with HCl gas (51) in AcOH (11), gives (80% yield (4)) 1,3-dichloropropanol-2 ("α-dichlorohydrin") (3:5985).]

With HBr. [ $\bar{C}$  with const.-boilg. HBr ( $D = 1.48$ ) as directed (66) cf. (1) gives alm. quant. yield 1-bromo-3-chloropropanol-2 [Beil. I-365,  $I_1$ -(185),  $I_2$ -(385)], b.p. 197° at 760 mm. (66), 92° at 20 mm. (66),  $D_4^{20} = 1.726$  (67),  $n_D^{25} = 1.5140$  (67) (corresp. bis-(N-phenylcarbamate), m.p. 73° (68))] (See below under reactn. of  $\bar{C}$  with metal bromides.)

With HI. [ $\bar{C}$  with 66% HI (69) cf. (66) (1) gives 3-chloro-1-iodopropanol-2 [Beil. I-366,  $I_1$ -(186),  $I_2$ -(386)], b.p. 226° (1), 107° at 19 mm. (66), 110° at 9 mm (69).] (See also below under behavior of  $\bar{C}$  with metal iodides.)

Behavior of  $\bar{C}$  with oxygenated inorganic acids. [ $\bar{C}$  with conc.  $H_2SO_4$  (70) or 84%  $H_2SO_4$  in cold (71) gives a corresp. mono (acid sulfate) ester [Beil. I-474,  $I_2$ -(538)], but whether this  $HSO_4$  group is attached through oxygen to the first or second carbon atoms of  $\bar{C}$  is unknown.]

[ $\bar{C}$  with  $HNO_3$  at not above 20° as directed (73) gives 42% yield of a mononitrate ester of 3-chloropropanediol-1,2 ("α-monochlorohydrin");  $\bar{C}$  with fuming  $HNO_3$  at 0° gives (74) γ-chloropropylene glycol dinitrate [Beil. I-474];  $\bar{C}$  with mixed  $HNO_3 + H_2SO_4$  gives (75) a mixed nitrous/nitric ester [Beil. I-474] of 3-chloropropanediol-1,2 (3:9038).]

[For analogous reactns. of  $\bar{C}$  with  $H_3PO_4$  (71) (89) or with  $HClO_4$  in ether (76) see indic. refs.; for behavior of  $\bar{C}$  toward HOCl see (77).]

Behavior of  $\bar{C}$  with salts of inorganic acids. (For behavior with NaCN, etc., see below under organic reactants.)

With metal chlorides. [ $\bar{C}$  in dry ether adds anhydrous  $ZnCl_2$  giving (78)  $ClCH_2CH(OZnCl)CH_2Cl$ ;  $\bar{C}$  in dry ether adds anhydrous  $MgCl_2$  giving (78)  $ClCH_2CH(OMgCl)CH_2Cl$ ; both these cpds. on hydrolysis yield (78) 1,3-dichloropropanol-2 ("α-dichlorohydrin") (3:5985). — Note also that  $\bar{C}$  (2 g.) with  $MgCl_2$  (1 g.) + aq. (2 ml.) + abs. alc. (5 ml.) in st. at 125° for 6 hrs. (79) cf. (11) gives  $Mg(OH)_2 + 1,3$ -dichloropropanol (above);  $\bar{C}$  with alc.  $FeCl_3$  gives (11)  $Fe(OH)_3 + 1,3$ -dichloropropanol-2 (above).] (See also below under reactn. of  $\bar{C}$  with  $RMgX$  cpds.)

With metal bromides. [ $\bar{C}$  (1 mole) with  $MgBr_2$  (1 mole) in dry ether gives (80) similarly  $ClCH_2CH(OMgBr)CH_2Br$  which on hydrolysis yields (80) 1-bromo-3-chloropropanol-2 (props. given above under reactn. of  $\bar{C}$  with HBr).] (See also below under reactn. of  $\bar{C}$  with  $RMgX$  cpds.)

With metal iodides. [ $\bar{C}$  with dry KI in st. at 100° for several days (1), or  $\bar{C}$  with KI (2 moles) in abs. alc. at 80-85° for 11 hrs. (81), or  $\bar{C}$  with NaI (1 mole) in acetone refluxed 21 hrs. (82), gives (40% yield (82)) 3-iodo-1,2-epoxypropane ("α-epiodohydrin") [Beil. XVII-10], b.p. 167° (1), 64° at 24 mm. (82), 62° at 24 mm. (81).]

[ $\bar{C}$  with conc. aq.  $MgI_2$  soln. gives alm. quant. yield (179) 3-chloro-1-iodopropanol-2 for whose constants see above under behavior of  $\bar{C}$  with HI.]

With alkali sulfides. [For patents on behavior of  $\bar{C}$  with aq.  $Na_2S$  see (83) (84).] (See also below.)

With alkali sulfites. [ $\bar{C}$  with  $NaHSO_3$  in s.t. nt  $100^\circ$  (11) or htd. under reflux (85) (46) (80) or in cold (87) gives sodium salt of 3-chloro-2-hydroxy-*n*-propyl hydrogen sulfite [Beil. I-474, I<sub>2</sub>-(538)].]

[ $\bar{C}$  (1 mole) with conc. aq.  $Na_2SO_3$  (2 moles) htd. under reflux  $1\frac{1}{2}$ -2 hrs. (46) or  $\bar{C}$  with conc. aq.  $K_2SO_3$  (85) gives corresp. salts of "glycerol disulfonic acid."]

[For behavior of  $\bar{C}$  with  $Na_3PO_4$  (15), with  $Na_2HPO_4$  (88), or with  $Na_3AsO_3$  (90) see indic. refs.]

Behavior of  $\bar{C}$  with other non-nitrogenous inorganic reactants. [ $\bar{C}$  with  $PCl_3$  gives an addition prod. (91) which with aq. regenerates  $\bar{C}$  and also forms  $HI_3PO_3$ . —  $\bar{C}$  with  $PCl_5$  yields (1) 1,2,3-trichloropropane (3:5840) +  $POCl_3$ .]

[ $\bar{C}$  with  $S_2Cl_2$  gives (92) 67% 1,3-dichloropropanol-2 ("α-dichlorohydrin") (3:5085) + 33% α,α'-dichloroacetone (3:0503). —  $\bar{C}$  with  $SO_2Cl_2$  +  $AlCl_3$  in  $CCl_4$  gives (93) β,β'-dichloroisopropyl chlorosulfonate.]

[ $\bar{C}$  in alk. soln. treated with  $HS$  at  $0^\circ$  gives (94) β-chloro-α-hydroxy-*n*-propyl mercaptan, b.p.  $60^\circ$  at 1.3 mm.,  $D_4^{20} = 1.2081$ ,  $n_D^{20} = 1.5257$  (94); at  $50^\circ$ , however, further loss of  $HCl$  occurs yielding by ring closure (94) β-hydroxytrimethyleno sulfide, b.p.  $57^\circ$  at 1.3 mm.,  $D_4^{20} = 1.2130$ ,  $n_D^{20} = 1.5433$  (94). — Note, however, that  $\bar{C}$  treated directly at  $125^\circ$  with  $HS$  gives (95) bis-(β-chloro-α-hydroxy-*n*-propyl) sulfide, oil, undistillable without decn. oven at 2 mm. (95).]

[ $\bar{C}$  with  $AsCl_3$  gives (96) tris-(β,β'-dichloroisopropyl)arsine, b.p.  $88-93^\circ$  at 10 mm.,  $D_4^{10} = 2.145$  (96).]

Behavior of  $\bar{C}$  with  $NH_3$  and other inorganic nitrogen cpds. [ $\bar{C}$  satd. repeatedly with  $NH_3$  gas as directed (97) gives tris-(β-chloro-α-hydroxy-*n*-propyl)amino [Beil. IV-291], m.p.  $92-93^\circ$  (corresp.  $\bar{B} \cdot HCl$ , m.p.  $173^\circ$  (97)); note that from the reactn. prod. of  $\bar{C}$  with ethyl neocacetate treatment with excess alc.  $NH_3$  gives (98) 3-chloro-2-(1?)-aminopropanol-1 (2?) [Beil. IV-291].]

[ $\bar{C}$  in alc. with  $NH_3$  gas or  $\bar{C}$  in alc. with  $NaNH_2$ , or  $\bar{C}$  with aq.  $NH_4OH$  (11) (99) gives a reactn. prod. of undetermined constitution, useful in productn. (100) of vat dyo printing pastes.]

[ $\bar{C}$  with hydrazine hydrate at  $100^\circ$  for 30 min. or in alc. under reflux for 5 hrs. gives (101) γ-hydrazinoepihydrin which with  $ZnCl_2$  at  $100^\circ$  gives (101) pyrazole [Beil. XXIII-39, XXIII<sub>1</sub>-(15)], m.p.  $69.5-70^\circ$  (101).]

[For behavior of  $\bar{C}$  with basic potassium iminodisulfonate,  $KN(SO_3K)_2$ , leading to dipotassium epihydrin-*N,N*-disulfonate (102) (103), or with basic potassium hydroxyl-aminodisulfonate,  $KON(SO_3K)_2$ , leading to dipotassium epihydrinhydroxylamine-*N,N*-disulfonate (104), see indic. refs.]

## CHEMICAL BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

### BEHAVIOR OF $\bar{C}$ WITH HYDROXY AND MERCAPTO COMPOUNDS

With monohydric alcohols.  $\bar{C}$  with alcohols reacts to give by opening of the oxide ring the corresp. primary ethers of 3-chloropropanediol-1,2 ("α-monochlorohydrin") (3:9038).

[ $\bar{C}$  with  $MeOH$  (1:0120) in pres. of  $H_2SO_4$  (105) (86) (106) (107), or  $\bar{C}$  with  $MeOH$  at elev. temp. under press. (108), or  $\bar{C}$  with  $MeOH$  +  $BF_3$  (109), gives (yields: 88-90% (105), 89% (106), 74.5% (109)) γ-chloro-β-hydroxy-*n*-propyl methyl ether ("chloromethylia") [Beil. I<sub>2</sub>-(538)], b.p.  $173^\circ$  at 752 mm. (105),  $172^\circ$  (106),  $170.5-171.5^\circ$  (109),  $95^\circ$  at 20 mm. (106),  $D_4^{20} = 1.1618$  (109),  $n_D^{20} = 1.4474$  (109). — Note, however, that  $\bar{C}$  with  $MeOH$  in pres. of  $KOH$  gives (110) (111) glycerol α,α'-dimethyl ether (β,β'-dimethoxy-isopropyl alc.)

[Beil. I-512, I<sub>2</sub>-(590)], b.p. 167-168° at 760 mm., 65.5-66.0° cor. at 9 mm. (113),  $D_4^{20} = 1.0085$  (113),  $D_4^{25} = 1.012$  (111),  $n_D^{25} = 1.4183$  (111),  $n_D^{20} = 1.4192$  (113) (corresp. *p*-nitrobenzoate, m.p. 43° (112)).]

[ $\bar{C}$  with EtOH (1:6130) in pres. of  $H_2SO_4$  refluxed 6 hrs. (17) or 20 hrs. (106) gives (yields: 80% (106), 76% (17))  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl ethyl ether ("chloroethylin") [Beil. I-474, I<sub>2</sub>-(538)], b.p. 183-184° (106), 104-106° at 60 mm. (17), 95-100° at 20 mm. (106),  $D_4^{25} = 1.107$  (17),  $n_D^{25} = 1.442$  (17). — Note, however, that  $\bar{C}$  with EtOH + KOH gives (110) glycerol  $\alpha,\alpha'$ -diethyl ether ( $\beta,\beta'$ -diethoxyisopropyl alc.) [Beil. I-512], b.p. 191° at 760 mm. (13) (111), 103-109° at 60 mm. (111), 61.5-62.0° cor. at 2 mm. (113),  $D_4^{25} = 0.952$  (111) (13),  $D_4^{20} = 0.9514$  (113),  $n_D^{25} = 1.419$  (111) (13),  $n_D^{20} = 1.4200$  (113).]

[For corresp. behavior of  $\bar{C}$  with *n*-butyl alc. (1:6180) +  $H_2SO_4$  (106), with isoamyl alc. (1:6200) +  $H_2SO_4$  (106), see indie. refs. —  $\bar{C}$  with dodecanol-1 (lauryl alc.) (1:5900) +  $FeCl_3$  in s.t. at 160° for 18 hrs. (39% yield (114)) or with  $H_2SO_4$  (115) gives  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl *n*-dodecyl ether, b.p. 157° at 1 mm. (114),  $n_D^{25} = 1.4525$  (114). — (For attempts to effect analogous reactn. between  $\bar{C}$  and *ter*-butyl alcohol (1:6140) in pres. of  $H_2SO_4$  and for physical constants on higher members of di(alkoxy)isopropyl alc. series see (113) )]

[ $\bar{C}$  with ethylene chlorohydrin (3:5552) +  $H_2SO_4$  gives (70% yield (116))  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl  $\beta$ -chloroethyl ether, b.p. 123-125° at 18 mm. (116).]

With polyhydric alcohols. [ $\bar{C}$  with ethylene glycol (1:6465) +  $H_2SO_4$  gives (56% yield (117))  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl  $\beta$ -hydroxyethyl ether, b.p. 135-139° (117).]

[For presumably analogous behavior of  $\bar{C}$  with glycerol +  $H_2SO_4$  see (118); for behavior of  $\bar{C}$  with cellulose + 50% NaOH see (119).]

With mercaptans.  $\bar{C}$  with mercaptans behaves in general analogously to  $\bar{C}$  with monohydric alcs. +  $H_2SO_4$ .

[E.g.,  $\bar{C}$  with MeSH is unreported. —  $\bar{C}$  with EtSH at 50° for 4 hrs. gives (90% yield (95))  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl ethyl sulfide, b.p. 114-115° at 16 mm.; note, however, that  $\bar{C}$  with EtSH in aq. KOH (i.e., KSEt) reacts differently yielding (95) 1,2-epoxy-*n*-propyl ethyl sulfide, b.p. 67-68° at 15 mm.,  $D_4^{22} = 1.0196$ ,  $n_D^{22} = 1.4789$ . —  $\bar{C}$  with *n*-PrSH + activated carbon at 90° for 7 hrs. gives (95)  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl *n*-propyl sulfide, b.p. 95° at 4 mm.]

[ $\bar{C}$  (1 mole) with benzyl mercaptan (1 mole) at 130° for 7 hrs. gives (95)  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl benzyl sulfide, b.p. 154-156° at 4 mm.; note, however, that  $\bar{C}$  (1 mole) with benzyl mercaptan (2 moles) in alc. NaOH gives (46) bis-( $\beta,\beta'$ -dibenzylmercapto)-isopropyl alc., m.p. 59°.]

[ $\bar{C}$  with thiophenol at 130° for 5 hrs. gives (95)  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl phenyl sulfide, b.p. 141° at 4 mm.]

With monohydric phenols.  $\bar{C}$  with monohydric phenols reacts to give by opening of the oxide ring the corresp. primary aryl ethers of 3-chloropropanediol-1,2 ("α-monochlorohydrin") (3.903S).

[ $\bar{C}$  with phenol (1:1420) (2 moles) at 110° for 10 hrs. (17), or at 150-160° under press. (120) (121) cf. (122), gives (86% yield (17))  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl phenyl ether ("α-monochlorohydrin  $\gamma$ -phenyl ether") [Beil. VI-147, VI<sub>1</sub>-(85)], b.p. 155-156° at 16 mm. (123), 152-153° at 12 mm. (121), 125-126° at 2 mm. (17),  $D_4^{25} = 1.209$  (17),  $n_D^{25} = 1.540$  (17) (this prod. is also formed even in pres. of a very little NaOH (123)). —  $\bar{C}$  (1 mole) with phenol (1:1420) (1 mole) + aq. NaOH (1¼ moles) at ord. temp. for 24 hrs. gives (10% yield (17) (125)) (124) 3-phenoxy-1,2-epoxypropane (glycidol phenyl ether) [Beil. XVII-105, XVII<sub>1</sub>-(56)], b.p. 213-244° cor. (124), 133° at 23 mm. (124), 115-116° at 3-4 mm. (17),  $D_4^{25} = 1.10$  (17), this reactn. occurs so readily that this prod. has formerly been mistaken for glycerol  $\alpha,\gamma$ -diphenyl ether (see following). —  $\bar{C}$  with phenol (1:1420) +

alc. NaOEt under reflux (120) cf. (124) (127) yields glycerol  $\alpha,\alpha'$ -di(phenyl) ether ( $\beta,\beta'$ -diphenoxisopropyl alc.) [Beil. VI-149, VI-1-(86)], lfts. from alc., m.p. 82° (120) (127), 81-82° (124), 80-81° (17).]

$\bar{C}$  (1 mole) with *p*-nitrophenol (1 mole) + aq. NaOH ( $1\frac{1}{2}$  moles) at ord. temp. for some days gives (120) 3-(*p*-nitrophenoxy)-1,2-epoxypropane (glycidol *p*-nitrophenyl ether) [Beil. XVII-1-(61)], m.p. 67° cor. (126), 69° (127). —  $\bar{C}$  (1 mole) with 2,4-dinitrophenol (1 mole) in aq. KOH (1 mole) refluxed several days, or  $\bar{C}$  with Ag 2,4-dinitrophenolate in alc., gives (42-47% yield) (note that  $\bar{C}$  is in excess (128)) glycerol  $\alpha,\alpha'$ -bis-(2,4-dinitrophenyl)ether, m.p. 70° (128).]

$\bar{C}$  (1 mole) with *o*-cresol (1:1400) (1 mole) + very dil. aq. NaOH at ord. temp. 9 days gives (30% yield (123))  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl *o*-tolyl ether ("  $\alpha$ -monochlorohydrin  $\gamma$ -(*o*-tolyl) ether) [Beil. VI-1-(201)], oil, b.p. 165° at 14 mm. (corresp. *N*-phenylcarbamate, m.p. 113-114°);  $\bar{C}$  (1 mole) with *o*-cresol (1 mole) + excess aq. NaOH at ord. temp. 4 days gives (131) 3-(*o*-toloxy)-1,2-epoxypropane (glycidol *o*-cresyl ether) [Beil. XVII-105], oil, b.p. 134.5° at 14 mm. (131); note, however, that  $\bar{C}$  (1 mole) with *Nn o*-cresolate (2 moles) in alc. refluxed 24 hrs. gives (37% yield (120)) cf. (130) glycerol  $\alpha,\alpha'$ -bis-(*o*-tolyl)ether [Beil. VI-354], m.p. 36-37°, b.p. 226° at 13 mm. (129) (130). —  $\bar{C}$  (1 mole) with *m*-cresol (1:1730) (1 mole) + 20% aq. NaOH ( $1\frac{1}{4}$  mole) at ord. temp. for 50 days gives (67.6% yield (126))  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl *m*-tolyl ether ("  $\alpha$ -monochlorohydrin "  $\gamma$ -(*m*-tolyl) ether) [Beil. VI-1-(186)], b.p. 167.5° cor. at 13 mm. (corresp. *N*-phenylcarbamate, m.p. 108-108.5° cor.);  $\bar{C}$  (1 mole) with *m*-cresol (1 mole) + excess aq. NaOH at ord. temp. gives (126) 3-(*m*-toloxy)-1,2-epoxypropane (glycidol *m*-tolyl ether) [Beil. XVII-1-(51)], b.p. 139.5-140° cor. at 15 mm.; note, however, that  $\bar{C}$  (1 mole) with *Nn m*-cresolate (2 moles) in alc. refluxed several days gives (23% yield (129)) (130) glycerol  $\alpha,\alpha'$ -bis-(*m*-tolyl) ether [Beil. VI-378], b.p. 232° at 13 mm. (129) (130). —  $\bar{C}$  (1 mole) with *p*-cresol (1:1410) (1 mole) + 20% aq. NaOH ( $1\frac{1}{2}$  mole) at ord. temp. for 8 days gives (47% yield (123))  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl *p*-tolyl ether ("  $\alpha$ -monochlorohydrin "  $\gamma$ -(*p*-tolyl) ether) [Beil. VI-1-(201)], oil, b.p. 105° at 14 mm. (corresp. *N*-phenylcarbamate, m.p. 113-114°);  $\bar{C}$  (1 mole) with *p*-cresol (1 mole) + excess aq. NaOH at ord. temp. gives (124) cf. (120) 3-(*p*-toloxy)-1,2-epoxypropane, (glycidol *p*-cresyl ether) [Beil. XVII-105, XVII-1-(61)], b.p. 136° at 17 mm. (124); note, however, that  $\bar{C}$  (1 mole) with *Na p*-cresolate in alc. under reflux gives (120) (124) glycerol  $\alpha,\alpha'$ -bis-(*p*-tolyl) ether [Beil. VI-395], m.p. 88° (120) (124).]

[The analogous behavior of  $\bar{C}$  with other monohydric phenols cannot be detailed here; however, for  $\bar{C}$  with  $\alpha$ -naphthol (1:1500) (120) (126) (132),  $\beta$ -naphthol (1:1640) (126) (127) (132), carvacrol (1:1760) (126), thymol (1:1430) (126), guaiacol (1:1405) (126) (127) see indie. refs.]

With dihydric phenols. [ $\bar{C}$  (1 mole) with pyrocatechol (1:1520) (1 mole) + KOH (1 mole) condenses with ring closure yielding (133) (134) 5-(hydroxymethyl)-2,3-benzodioxane-1,4, m.p. 96°, b.p. 160° at 17 mm. (133) (134).]

[For behavior of  $\bar{C}$  with 4-acetylresorcinol (resacetophenone) see (135).]

#### BEHAVIOR OF $\bar{C}$ WITH ETHERS

[ $\bar{C}$  with dimethyl ether +  $\text{BF}_3$  at -35° after reactn. and distn. gives (86.6% yield (136)) *tris*-( $\beta$ -chloro- $\beta'$ -methoxy-isopropyl) borate, accompanied by a little  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl methyl ether (for constants see above under behavior of  $\bar{C}$  with monohydric alcs.). —  $\bar{C}$  with diethyl ether +  $\text{BF}_3$  at 20-25° overnight followed by treatment with aq. 2*N*  $\text{Na}_2\text{CO}_3$  gives mainly (136)  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl ethyl ether (for constants see above under behavior of  $\bar{C}$  with monohydric alcs.) accompanied by ethyl alcohol (1:6130); direct distillation of the reaction mixt. without  $\text{Na}_2\text{CO}_3$  treatment, however,

gives (136) *tris*-( $\beta$ -chloro- $\beta$ -ethoxyisopropyl) borate, b.p. 210–216° at 12 mm.,  $D_4^{22} = 1.148$  (126).]

[ $\bar{C}$  with  $\alpha$ -halogen-methyl alkyl ethers in pres. of  $HgCl_2$  gives (137) (105) (by ring opening and addn.) mixed formals; e.g.,  $\bar{C}$  with chloromethyl methyl ether (3:7085) +  $HgCl_2$  gives formaldehyde  $\beta, \beta'$ -dichloroisopropyl methyl acetal, etc.]

#### BEHAVIOR OF $\bar{C}$ WITH CARBONYL COMPOUNDS

With aldehydes. [ $\bar{C}$  with aldehydes condenses to yield the corresp. 2-alkyl-4-(chloromethyl)-1,3-dioxolanes; (however, the prod. to be expected from  $\bar{C}$  with formaldehyde (1:0145), viz. 4-(chloromethyl)-1,3-dioxolane [Beil. XIX-8, XIX-1-(610)], b.p. 126° at 750 mm. (138), has not been so reported, but rather from 3-chloropropanediol-1,2 ("  $\alpha$ -monochlorohydrin") (3:9038)]; for behavior of this prod. with solid KOH at 110° involving loss of HCl and formn. (94% yield (139)) (140) of the formal of propen-1-diol-2,3, b.p. 93–95° at 758 mm. (139),  $n_D^{20} = 1.4336$  (139), see indic. refs.]

[ $\bar{C}$  with acetaldehyde (1:0100) +  $SnCl_4$  in  $CCl_4$  at 18–25° gives (45% yield (141)) 4-(chloromethyl)-2-methyl-1,3-dioxolane ("acetaldehyde  $\gamma$ -chloropropylene acetal") [Beil. XI-XI-1-(610)], h.p. 158–162° at 760 mm. (141). —  $\bar{C}$  with propionaldehyde (1:0110) +  $SnCl_4$  in  $CCl_4$  gives (64% yield (141)) (142) 4-(chloromethyl)-2-ethyl-1,3-dioxolane, h.p. 65–70° at 18 mm. (142). — For analogous reactions of  $\bar{C}$  with *n*-butyraldehyde, octanal-1, decanal-1, and dodecanal-1 see (142); with crotonaldehyde see (141).]

With ketones.  $\bar{C}$  with ketones condenses in completely analogous fashion to yield the corresp. 2,2-dialkyl-1,3-dioxolanes. [E.g.,  $\bar{C}$  (converted to 3-chloropropanediol-1,2 ("  $\alpha$ -monochlorohydrin") (3:9038) although this may be unnecessary) gives (60% yield (58)) 4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane ("acetone-glycerol  $\alpha$ -chlorohydrin"), b.p. 157° at 767 mm.,  $D_4^{20} = 1.1079$ ,  $n_D^{25} = 1.43750$  (58). —  $\bar{C}$  with benzophenone (1:5150) +  $SnCl_4$  in  $CCl_4$  at 13–25° gives (73% yield (141)) 4-(chloromethyl)-2,2-diphenyl-1,3-dioxolane, m.p. 44.5°, b.p. 159–167° at 2–3 mm. (141). — For analogous behavior of  $\bar{C}$  with phenacyl bromide, camphor, and cyclopentadecanone see (141).]

#### BEHAVIOR OF $\bar{C}$ WITH ORGANIC ACIDS

(For salts, acid chlorides, acid anhydrides, see below.)

With aliphatic monobasic acids. [ $\bar{C}$  with AcOH (1:1010) in s.t. at 180° for 24 hrs. (143) cf. (1) gives a mixt. of both glycerol  $\alpha$ -chlorohydrin  $\alpha'$ -acetate (3:6775) and glycerol  $\alpha$ -chlorohydrin  $\beta$ -acetate (3:6517);  $\bar{C}$  with AcOH + a little  $FeCl_3$  at room temp. for 24 hrs. gives (90% yield (144)) a prod. supposed originally (144) to be glycerol  $\alpha$ -chlorohydrin  $\alpha'$ -acetate (3:6775); note, however, that later workers (36) could obtain only 25% yield unless mixt. stood 15 days at room temp. or 2 days at 80° and regarded the product as glycerol  $\alpha$ -chlorohydrin  $\beta$ -acetate (3:6517). —  $\bar{C}$  with aliphatic monobasic acids contg. at least 4 carbon atoms +  $AlCl_3$  (145) or  $\bar{C}$  with aliphatic, alicyclic, or aromatic acids (contg. no sulfonic acid groups) + pyridine (146) gives corresp. mono esters (probably mixt. of  $\alpha$ - and  $\beta$ -) of 3-chloropropanediol-1,2 (3:9038).]

[ $\bar{C}$  with trichloroacetic acid (3:1150) undergoes ring closure (similar to that of  $\bar{C}$  with carbonyl cpds. above) giving (147) 4-(chloromethyl)-2-hydroxy-2-(trichloromethyl)-1,3-dioxolane, b.p. 99–101° at 0.11 mm.,  $n_D^{23} = 1.4892$ .]

[ $\bar{C}$  with thiolacetic acid ( $CH_3CO.SH$ ) at 60° for 12 hrs. gives (76% yield (148))  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl thiolacetate, b.p. 100–101° at 1 mm.,  $D_4^{20} = 1.2806$ ,  $n_D^{20} = 1.5186$ ; on longer hgt., e.g., 35 hrs. at 60°, or even at ord. temp. on 2 weeks stgd. in diffuse light, largely reart. to  $\beta$ -chloro- $\beta$ -mercapto-isopropyl acetate, b.p. 69–70° at 1 mm.,  $D_4^{20} = 1.2308$ ,  $n_D^{20} = 1.4555$  (148).]



With HCN (or its salts).  $\bar{C}$  with excess anhydrous HCN in s.t. at 75–85° for 90 hrs. (149) (150) cf. (151) (152), or  $\bar{C}$  with anhydrous HCN + some solid KCN in s.t. at ord. temp. for 3–4 days (153), or  $\bar{C}$  with aq.  $\text{Ca}(\text{CN})_2$  (154), gives (yields: 85% (153), 72% (150), 70% (151), 65% (149))  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-butyronitrile [Beil. III-310], b.p. 250° dec. (151), 140° at 20 mm. (151), 134–135° at 15 mm. (153), 110–111° at 2 mm. (151),  $D_{20}^{25} = 1.233$  (153),  $n_D^{25} = 1.4735$  (153). — Note, however, that  $\bar{C}$  with aq. or alc. KCN splits out KCl giving (155) (85) 3-cyano-1,2-epoxypropane ("epicyanhydrin") [Beil. XVIII-261], m.p. 162°.]

#### BEHAVIOR OF $\bar{C}$ WITH SALTS OF ORGANIC ACIDS

$\bar{C}$  with dry KOAc first at 110°, later at 150° (156) cf. (157), or at 120–135°, later 150° (18) (158), gives 3-acetoxy-1,2-epoxypropane (glycidyl acetate) [Beil. XVII-106], b.p. 168–169° (157), 167–168° (143), 162–164° at 750 mm. (158), accompanied by other prods. (for study of polymerization of this prod. see (18) (158).)]

$\bar{C}$  with aq. K cyanate on boilg. (159) (160) or  $\bar{C}$  with free isocyanic acid (from btg. cyanuric acid) in cold (160) adds yielding 5-(chloromethyl)oxazolidone-2 [Beil. XXVII-145, XXVII<sub>1</sub>-(200)], pr. from aq.,  $\text{C}_6\text{H}_6$ , or  $\text{Ac}_2\text{O}$ , m.p. 106° (161) (159), 105° (159).

[For behavior of  $\bar{C}$  with disodium methyl phosphate (162) or with disodium glycerophosphate (163) see indic. refs.]

#### BEHAVIOR OF $\bar{C}$ WITH ACID CHLORIDES

$\bar{C}$  with acid chlorides yields corresp. esters of  $\beta,\beta'$ -dichloroisopropyl alc. ("glyceml  $\alpha$ -dichlorohydrin") (3:5985) as exemplified by the following illustrations.

With aliphatic acid chlorides.  $\bar{C}$  with  $\text{AcCl}$  (3:7065) (164) in s.t. at 100° for 2 hrs. (165) or 30 hrs. (160) gives (73% yield (164))  $\beta,\beta'$ -dichloroisopropylacetate (3:6318). —  $\bar{C}$  with propionyl chloride (3:7170) in s.t. at 135° for 3 hrs. gives (167)  $\beta,\beta'$ -dichloroisopropyl propionate [Beil. II<sub>2</sub>-(221)], h.p. 208°,  $D_{20}^{20} = 1.2222$  (167). —  $\bar{C}$  with *n*-butyryl chloride (3:7370) in s.t. at 100° (166) or with exclusion of aq. in flask at 75° for 8 hrs. (167) gives  $\beta,\beta'$ -dichloroisopropyl *n*-butyrate [Beil. II-271, II<sub>2</sub>-(246)], h.p. 226–227° at 738 mm. (166), 223.5° (167),  $D_{20}^{20} = 1.1792$  (167),  $n_D^{20} = 1.4540$  (167). —  $\bar{C}$  with isovaleryl chloride (3:7560) gives (166) (168)  $\beta,\beta'$ -dichloroisopropyl isovalerate [Beil. II-312, II<sub>2</sub>-(275)], h.p. 245° at 737 mm. (166), 127–140° at 36 mm. (168),  $D_{20}^{20} = 1.444$  (168),  $n_D^{20} = 1.450$  (168). —  $\bar{C}$  with stearoyl chloride (3:9960) in s.t. at 130° for 3½ hrs. gives (167)  $\beta,\beta'$ -dichloroisopropyl stearate [Beil. II<sub>2</sub>-(352)], m.p. 39.5°.]

#### BEHAVIOR OF $\bar{C}$ WITH ACID ANHYDRIDES

With anhydrides of aliphatic acids.  $\bar{C}$  with  $\text{Ac}_2\text{O}$  (1:1015) in s.t. at 180° for 4 hrs. (166) or  $\bar{C}$  with  $\text{Ac}_2\text{O} + \text{FeCl}_3$  at ord. temp. for 24 hrs. (144) gives (90% yield (144))  $\beta,\beta'$ -dichloroisopropyl acetate (3:6318).]

With anhydrides of aromatic acids.  $\bar{C}$  with phthalic anhydride (1:0725) + dimethylaniline at 100° is claimed (169) to give the monomolecular neutral phthalate [Beil. XIX-165] of 3-chloropropanediol-1,2.]

#### BEHAVIOR OF $\bar{C}$ WITH ORGANO METALLIC COMPOUNDS (OR THEIR EQUIVALENTS)

Behavior with Grignard compounds. With  $\text{RMgX}$  cpds. from alkyl or alkaryl halides  $\bar{C}$  with  $\text{MeMgI}$  in dry ether evolves gas ( $\text{CH}_4$ ?) and after acidification yields (171) 3-chloro-1-iodopropanol-2 (for constants see above under behavior of  $\bar{C}$  with HI).]

[The reactn. of  $\bar{C}$  with  $\text{EtMgBr}$  may give three different prods. (or mixtures of them) according to circumstances: the first of these is 1-bromo-3-chloropropanol-2 (for constants

see above under behavior of  $\bar{C}$  with  $HBr$ ; the second is the expected 1-chloropentanol-2 (3:8225); the third is cyclopropanol, b.p. 100-103° (80) (172),  $D_4^{20} = 0.9110$  (80),  $n_D^{20} = 1.4129$  (80) (corresp. *p*-nitrobenzoate, m.p. 72.0-72.5°; 3,5-dinitrobenzoate, m.p. 108-109°; *N*-phenylcarbamate, m.p. 101.5-102.0°; *N*-(*p*-nitrophenyl)carbamate, m.p. 159-160°; *N*-( $\alpha$ -naphthyl)carbamate, m.p. 100.5-101.5° (172)). — Note that  $\bar{C}$  with  $EtMgBr$  gives (16-19% yield (67) (173)) 1-chloropentanol-2 (3:8225), while  $\bar{C}$  with  $MgEt_2$  gives 70-83% yield (80). — For review of earlier work on this rather complex system see (80) (173) (67).]

[For behavior of  $\bar{C}$  with 15 other  $RMgX$  epds. leading in general to chlorohydrins of type  $RCH_2CH(OH)CH_2Cl$  see (173).]

With  $RMgX$  epds. from *aryl halides*. [ $\bar{C}$  with  $C_6H_5MgBr$  gives (18% yield (173)) (132) (174) (175) 3-chloro-1-phenyl-propanol-2 [Beil. VI-503], b.p. 254-257° (174), 153-154° at 28 mm. (174) (175), 142-144° at 23 mm. (173),  $D_4^{25} = 1.1528$  (173),  $n_D^{25} = 1.5470$  (173) (corresp. 3,5-dinitrobenzoate, m.p. 120-121° (173)). — For analogous behavior of  $\bar{C}$  with  $RMgX$  epds. from  $\alpha$ -bromonaphthalene and from *p*-bromanisole (*p*-bromophenyl methyl ether) see (132).]

Behavior with various sodio derivatives. [ $\bar{C}$  with diethyl sodiomalonate in abs. alc. at 50° does not split out  $NaCl$  but rather by ring opening, addn. of reactant, and elimination of  $EtOH$  ppts. (176) (177) cf. (178) the monosodium enolate (m.p. 172° dec. (176)) of  $\alpha$ -carbethoxy- $\delta$ -chloro-*n*-valero- $\gamma$ -lactone [Beil. XVIII-373, XVII-478], set free (yields: 78% (177), 50% (176)) by acidification as an oil, b.p. 180-182° at 12 mm. (176), 175-180° at 12 mm. (177). — Note that this lactone with excess alc.  $NH_3$  gives on evapn. (176) (179)  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propylmalondiamide [Beil. III-450], m.p. 117-118°.]

[ $\bar{C}$  with ethyl sodioacetacetate in abs. alc. at 50° does not split out  $NaCl$  but rather by ring opening, etc., as in preceding case gives after acidification (yields: 50% (176), 74% (177))  $\alpha$ -aceto- $\delta$ -chloro-*n*-valero- $\gamma$ -lactone [Beil. XVII-421, XVII-(230)], b.p. 108° at 16 mm. (177), 163° at 12 mm. (176).]

[ $\bar{C}$  with ethyl sodio-benzoylacetate in abs. alc. behaves in analogous fashion yielding after acidification (180)  $\alpha$ -benzoyl- $\delta$ -chloro-*n*-valero- $\gamma$ -lactone [Beil. XVII-497], m.p. 103-106°.]

#### BEHAVIOR OF $\bar{C}$ WITH AMINES

With primary amines. With *aliphatic primary amines*. This reactn. appears not to have been thoroughly studied (however, for reactn. of  $\bar{C}$  with  $MeNH_2$  (181) and use of prod. in prepn. of vat dye printing pastes (182) see indie. refs.).

With *cyclic primary amines*. [ $\bar{C}$  (1 mole) with cyclohexylamine (3½ moles) under reflux gives (18% yield (82))  $\beta,\beta'$ -bis-(cyclohexylamino)isopropyl alc., m.p. 72-73°.]

With *aromatic primary amines*. [ $\bar{C}$  (1 mole) with aniline (2 moles) in toluene refluxed 95 hrs. gives (yield not stated (71)) 3-(phenylamino)-1,2-epoxypropane ("glycidanilide"). —  $\bar{C}$  (1 mole) with aniline (3 moles) at 140° is claimed (183) to yield  $\beta,\beta'$ -bis-(phenylamino)isopropyl alc. [Beil. XII-553], m.p. 53-54°, but later workers could obtain only viscid oils (184) or a further reactn. prod. supposed (185) to be  $\beta$ -(phenylamino)- $\beta'$ -(di-phenylamino)isopropyl alc., m.p. 350° dec. (185).]

[ $\bar{C}$  (1 mole) with *p*-toluidine (2 moles) might be expected to yield 3-(*p*-tolylamino)-1,2-epoxypropane, but no such cpd. appears to have been recorded. — However,  $\bar{C}$  (1 mole) with *p*-toluidine (1 mole) in *dl.* alc. (186) (184) (52) (but not in  $C_6H_6$  (184)) opens ring to yield by addn.  $\beta$ -chloro- $\beta'$ -(*p*-tolylamino)isopropyl alc., m.p. 85° (184), 81-82° (186); this prod. on litg with *p*-toluidine (184) or  $\bar{C}$  (1 mole) with *p*-toluidine (2 moles) at 155° (186) gives  $\beta,\beta'$ -bis-(*p*-tolylamino)isopropyl alc., m.p. 116° (184), 113.5° (186).]

[ $\bar{C}$  with *p*-phenetidine hydrochloride in aq. soln. at ord. temp. especially in sunlight gives (40% yield (187)) cf. (188) *N,N'*-bis-( $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl)phenetidine.]

[For behavior of  $\bar{C}$  with  $\beta$ -naphthylamine in xylene under reflux (189), with arsanic acid (190), or with *p*-aminophenol (or its ethers) (191) see indio. refs.]

With heterocyclic primary amines.  $\bar{C}$  with  $\alpha$ -aminopyridine gives (63% yield (192)) by addn. to oxide ring and subsequent ring closure a prod., m.p. 190°, regarded as "1,2-divinylene-5-hydroxytetrahydropyrimidine."

With phenylhydrazine.  $\bar{C}$  with  $1\frac{1}{2}$  pts. phenylhydrazine in ether at not above 15° for 10 days ppt. phenylhydrazine hydrochloride and leaves in the ether 4-hydroxy-1-phenylpyrazolidine [Beil. XXIII-348], m.p. 103-104° (193); this prod. with phenylhydrazine hydrochloride on warming in  $C_6H_6$  (193) or  $\bar{C}$  with 2 pts. phenylhydrazine in  $C_6H_6$  refluxed 8-9 hrs. (194) gives (58% yield (194)) 1-phenylpyrazole [Beil. XXI-49, XXIII- (15)], b.p. 246.5° cor. at 765.4 mm. (194), m.p. 11-11.5° (191),  $D_4^{20} = 1.1127$  (195),  $n_D^{20} = 1.5066$  (195).]

With secondary amines. With aliphatic secondary amines.  $\bar{C}$  with  $Me_2NH$  presumably gives (196)  $\beta$ -chloro- $\beta'$ -(dimethylamino)isopropyl alc., but no constants are reported in the literature, either for it or for its ring-closure derivative, 3-(dimethylamino)-1,2-epoxypropane, cf. (196); note further that the prod. to be expected from  $\bar{C}$  + 2  $Me_2NH$ , viz.,  $\beta, \beta'$ -bis-(dimethylamino)isopropyl alc. [Beil. IV-290] (197), although known, has not been prepd. from  $\bar{C}$ , but only by other means.]

$\bar{C}$  with eq.  $Et_2NH$  gives (196) (198) cf. (199) 3-(diethylamino)-1,2-epoxypropane [Beil. XVIII-583], b.p. 155-159° at 760 mm. (198), 55-60° at 15 mm. (196), 40-50° at 8 mm. (198),  $D_4^{18} = 0.8876$  (196). —  $\bar{C}$  (1 vol.) with  $Et_2NH$  ( $3\frac{1}{2}$  vols.) refluxed 2-3 hrs. gives (82% yield (200))  $\beta, \beta'$ -bis-(diethylamino)isopropyl alc., b.p. 114° nt 9 mm. (corresp. B.2PkOH, m.p. 163° (200).]

$\bar{C}$  with di-*n*-propylamine (2 moles) gives (70% yield (215)) 1,3-bis-(di-*n*-propylamino)propanol-2, b.p. 99-191° at 3 mm.,  $D_4^{20} = 0.8624$ ,  $n_D^{20} = 1.4483$  (215).]

With aromatic secondary amines.  $\bar{C}$  with *N*-methylaniline gives (198) cf. (199) 3-(*N*-methylanilino)-1,2-epoxypropane, b.p. 160-162° at 30 mm. (198), 132-135° at 8 mm. (198); note, however, that  $\bar{C}$  (1 mole) with *N*-methylaniline (1 mole) at 100° for 4 hrs. (82) gave none of the preceding epd. but a very small yield (2%) of  $\beta, \beta'$ -bis-(*N*-methylanilino)isopropyl alc., m.p. 82°, accompanied by other prods.]

$\bar{C}$  with diphenylamine at 160-170° under press. splits out  $HCl$  and ring-closes with loss of  $H_2O$  yielding (201) 1-phenyl-3-hydroxy-1,2,3,4-tetrahydroquinoline [Beil. XXI- (205)], m.p. 79°, b.p. 200° at 5 mm.]

With heterocyclic secondary amines.  $\bar{C}$  with piperidine gives (196) (198) by elimination of  $HCl$  3-(piperidino)-1,2-epoxypropane, b.p. 86.5-88° at 15 mm. (196), 72-77° at 8 mm. (198),  $D_4^{16} = 0.9669$  (196).]

With tertiary amines.  $\bar{C}$  with tertiary amines gives quaternary salts, but this reaction is often followed by opening of the oxide ring and addn. of reactant.

With aliphatic tertiary amines.  $\bar{C}$  with alc.  $Et_3N$  (1 mole) in s.t. at 100° gives (202) a little of the corresp. quat. salt, viz., triethyl-( $\beta, \gamma$ -epoxy-*n*-propyl)ammonium chloride [Beil. XVIII-583]; note, however, that  $\bar{C}$  with alc.  $Et_3N$  (1 mole) in s.t. at 100° for 6 hrs. gives also (202) (203) 2-hydroxytrimethylene-1,3-bis-(triethyl-ammonium chloride) [Beil. IV-290] together with other prods.]

[For behavior of  $\bar{C}$  with *N,N*-dimethyl-"stenyl" amine see (204).]

With heterocyclic tertiary amines. [For study of behavior of  $\bar{C}$  with pyridine see (205) (200); with quinoline see (207).]

#### BEHAVIOR OF $\bar{C}$ WITH OTHER NITROGENOUS REACTANTS

(Note that in the following examples reaction occurs by opening of the oxide ring and that elimination of chlorine, if it occurs at all, is effected only in a subsequent ring closure.)

$\bar{C}$  (1 mole) with disodium cyanamide (1 mole) in aq. soln. at ord. temp. for 24 hrs. presumably first yields the sodium deriv. of *N*-( $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl)cyanamide, but this immediately ring-closes giving (33% yield (208)) 5-(chloromethyl)-2-amino-oxazoline, m.p. 142°.]

$\bar{C}$  (1 mole) with *p*-toluenesulfonanilide (1 mole) + a few drops pyridine at 120° reacts vigorously giving (56% yield (209)) *N*-( $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl)-*N*-phenyl-*p*-toluenesulfonamide, m.p. 96-97°; note that this prod. in boilg. alc. on treatment with NaOH loses HCl and ring-closes (92% yield (209)) to the corresp. *N*-( $\beta$ , $\gamma$ -epoxy-*n*-propyl)-*N*-phenyl-*p*-toluenesulfonamide, m.p. 77°.

$\bar{C}$  (1 wt. pt.) with phthalimide (1 wt. pt.) at 140-150° for 3 hrs. gives (35% yield on phthalimide (210)) cf. (211) (212) *N*-( $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl)phthalimide [Beil. XXI-1-(369)], m.p. 95.0-96.5° (210), 95-97° (213). — Note that *N*-( $\beta$ , $\gamma$ -epoxy-*n*-propyl)phthalimide ("phthalimidoepihydrin"), m.p. 93-94° (213), has been prepd. (75% yield (213)) from 3-bromo-1,2-epoxypropane ("epibromohydrin") with K phthalimide, and in  $\text{CHCl}_3$  with HCl gas or even directly with conc. HCl opens the oxide ring to give (213) the above *N*-( $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propyl)-phthalimide, m.p. 96-97° (213).]

### COLOR REACTION OF $\bar{C}$

Color reaction with pyridine (and pyridine bases).  $\bar{C}$  in MeOH with pyridine and/or various "pyridine bases" gives specific color reactions; these can be used for detection of "pyridine bases," e.g., in denatured alcohol and probably vice versa; for detailed study see (214).

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- (41) Stein, Flemming, 16, 1943; *C.A.* 38, 2666 (1939); French 843,841, für *Chimie* 1871, 252. (43) Smith, *Z. Physik. Chem.* 92, 739-740 (1917); 93, 83-85 (1919). (44) Claus, *Ber.* 19, 556-559 (1877). (45) Bartholot, *Ann. chim. (2)* 48, 206 (1858). 101, 67-68 (1857). (46) Fro, *Ber.* 21, 1290 (1888). (48) I 2677 (1891). (50) Bigot, *Ann. chim. (2)* 22, 444-445 (1891). (61) Hübner, Müller, *Ann.* 159, 184-187 (1871). (52) von Richter, *J. prakt. Chem.* (2) 20, 193-195 (1870). (53) Koelsch, *J. Am. Chem. Soc.* 52, 1106 (1930). (54) Tanoo, *Ber.* 68, 1342 (1935). (55) Cloez, *Ann. chim. (6)* 9, 170 (1886). (56) Grimaux, Adam, *Bull. soc. chim. (2)* 33, 257-259 (1880). (57) Cloez, *Ann. chim. (6)* 9, 206 (1886). (58) Fischer, Pfähler, *Ber.* 53, 1608 (1920). (59) Böseken, Hermans, *Bull. soc. chim. (4)* 39, 1254 (1926). (60) Hanriot, *Ann. chim. (5)* 17, 75 (1870). (61) Banerjee, Sen, *J. Indian Chem. Soc.* 9, 509-518 (1932). (62) Smith, Wode, Widhe, *Z. physik. Chem.* 139, 157-162 (1927). (63) Groll, Hearne (to Shell Development Co.), U.S. 2,086,077, July 1937. (64) Swarts, *Cent.* 1903, I 12; (b) Paterr II 541-544 (1891). (65) Blanchard, *Bull. soc. chim. (4)* 41, 825-826 (1927). (67) Koelsch, McElvain, *J. Am. Chem. Soc.* 51, 3390-3394 (1929). (68) Johnson, Langley, *Am. Chem. J.* 44, 358 (1910). (69) Ingold, Rothstein, *J. Chem. Soc.* 1931, 1671-1672. (70) Oppenheim, *Ber.* 3, 736 (1870). (71) Zetsche, Aeschlimann, *Helv. Chim. Acta* 9, 711-714 (1926). (72) Groll, Hearne (to Shell Development Co.), U.S. 2,106,347, Jan. 25, 1938; *Cent.* 1938, II 1676; *C.A.* 32, 2542-2543 (1938). (73) I.G., French 846,575, Sept. 20, 1939; *C.A.* 35, 1071 (1941). (74) Henry, *Ann.* 153, 166, 168-169 (1870). (75) Henry, *Ber.* 4, 703 (1871). (76) Hofmann, Zedwitz, Wagner, *Ber.* 42, 4391 (1909). (77) Carius, *Ann.* 134, 73-75 (1865). (78) Ribas, Tapia, *Anales soc. españ. fis. quim.* 28, 630-644 (1930). *Cent.* 1932, II 3862; *C.A.* 24, 4265 (1930). (79) Delaby, *Ann. chim. (9)* 29, 67-68 (1923). (80) Magrane, Cottle, *J. Am. Chem. Soc.* 64, 484-487 (1942). (81) Nel, *Ann.* 335, 237-238 (1904). (82) Wedekind, Bruch, *Ann.* 471, 78, 94, 95, 97 (1929). (83) Lumière, (88) Bailly, *Bull. soc. chim. (4)* 29, 274-280 (1921). (89) Cavalier, *Ann. chim. (7)* 18, 482-483 (1899). (90) Oechslein (to Etab. Poulenc Frères), Brit. 191,028, Feb. 14, 1923; *Cent.* 1923, IV 721; *C.A.* 17, 2887 (1923); French 656,366, July 19, 1923; *Cent.* 1923, IV 721; not in *C.A.* (91) Hanriot, *Bull. soc. chim. (2)* 22, 550-552 (1879). (92) Malinovskii, *J. Gen. Chem. (U.S.S.R.)* 9, 579-580 (1929). *C.A.* 24, 275 (1930). (93) Blanchard, *Bull. soc. chim. (4)* 41, 825-826 (1927). (94) Schiff, *Gazz. chim. ital.* 21, II 1-6 (1891). (95) Stallmann (to du Pont Co.), U.S. 1,977,251, Oct. 16, 1934; *Cent.* 1935, I 2603; *C.A.* 29, 352 (1935). (100) Stallman (to du Pont Co.), U.S. 1,977,250, Oct. 16, 1934; *Cent.* 1935, I 1619; *C.A.* 29, 352 (1935). (101) Traube, Dec. 17, 1920; *Cent.* 1921, I 101. (105) Blanchard, *Bull. soc. chim. (4)* 39, 1263-1265 (1926). (106) Fourneau, Ribas, *Bull. soc. chim. (4)* 39, 1504-1559 (1926). (107) I.G., Brit. 271,169, June 16, 1927; *Cent.* 1927, II 2110; *C.A.* 22, 1596 (1928). (108) I.G., French 697,786, Jan. 22, 1931; *Cent.* 1931, I 2394; [*C.A.* 25, 3013 (1931)]. (109) Petrov, *J. Gen. Chem. (U.S.S.R.)* 19, 1918-1922 (1940); *C.A.* 33, 3603 (1941). (110) Zunino, *Atti accad. Lincei* (5) 6, II 348 (1897). (111) Fairbourn, Gibson, Stephens, *J. Chem. Soc.* 1931, 450, 454. (112) Fairbourn, *J. Chem. Soc.* 1929, 1161-1152. (113) Henze, Rogers, *J. Am. Chem. Soc.* 61, 434-435 (1939). (114) Grummitt, Hall, *J. Am. Chem. Soc.* 66, 1229 (1944). (115) Henkel et Cie, French 744,749, April 26, 1933; *Cent.* 1933, II 2210; *C.A.* 27, 2242 (1933). (116) Fourneau, Ribas, *Bull. soc. chim. (4)* 41, 1053 (1927). (117) Kharsch, Nudenberg, *J. Org. Chem.* 8, 189 (1943). (118) Loehr (to I.G.), Ger. 510,422, Oct. 18, 1930; *Cent.* 1931, I 154; [*C.A.* 25, 964 (1931)]. (119) Dreyfus,

Brit. 166,767, Aug. 18, 1921; *Cent.* 1921, IV 1140; C.A. 16, 830 (1922). {120} Lindeman, *Ber.* 24, 2146-2148 (1891).

{121} Fischer, Krämer, *Ber.* 41, 2730 (1908). {122} Fournneau, *J. pharm. chim.* (7) 1, 58 (1910); *Cent.* 1910, I 1134; C.A. 4, 3070 (1910). {123} Boyd, Marle, *J. Chem. Soc.* 93, 839-841 (1908). {125} Böeseken, *Rec. trav. chim.* 34, 102 (1915). {126} Marle, *J. Chem. Soc.* 101, 305-317 (1912). {127} Fournneau (to Etab. Poulenc Frères), *Ger.* 228,205, Nov. 7, 1910, *Cent.* 1910, II 1790-1791, [C.A. 28, 2165 (1911)]. {128} Brenans, *Bull. soc. chim.* (4) 13, 529-530 (1913). {129} Boyd, *J. Chem. Soc.* 83, 1137-1138 (1903). {130} Boyd, Marle, *J. Chem. Soc.* 95, 1807-1808 (1909).

{131} Boyd, Knowlton, *J. Chem. Soc.* 95, 1503 (1909). {132} Fournneau, Trefouel, *Bull. soc. chim.* (4) 43, 454-458 (1928). {133} Fournneau, Maderin, LeStrange, *J. pharm. chim.* (8) 18, 185-191 (1933). *Cent.* 1934, I 391, C.A. 27, 5738 (1933). {134} Soc. Usines Chim. des Rhone-Poulenc, *Brit.* 420,978, Dec. 20, 1924, *Cent.* 1935, I 2216, [C.A. 29, 3468 (1935)]. *French* 770,485, Sept. 14, 1934, *Cent.* 1935, I 2216; C.A. 29, 477 (1935). {135} Nadkarni, Wheeler, *J. Chem. Soc.* 1936, 589-591. {136} Meerwein, Hinz, Hofmann, Kroning, Pfeil, *J. prakt. Chem.* (2) 147, 258-260, 268-273 (1936/7). {137} Blanchard, *Bull. soc. chim.* (4) 49, 281-289 (1931). {138} *Bull. soc. chim.* (3) 21, 276-277 (1899). {139} Fischer, Baer, Reldmann, *Ber.* 63, 1738-1739 (1930).

{140} Fischer, Baer, Pollock, Nidecker, *Helv. Chim. Acta* 20, 1214 (1937). {141} Willfang, *Ber.* 74, 145-153 (1941). {142} Bersin, Willfang, *Ber.* 70, 2167-2173 (1937). {143} Bigot, *Ann. chim.* (6) 23, 491, 493 (1891). {144} Knoevenagel, *Ann.* 402, 134-138 (1914). {145} Stein (to General Aniline and Film Corp.), U.S. 2,224,026, Dec. 3, 1940, C.A. 35, 1802 (1941). *Brit.* 509,072, Aug. 10, 1939, *Cent.* 1939, II 4351, C.A. 34, 2862 (1940). *French* 850,709, Dec. 23, 1939, C.A. 36, 1947 (1942). {146} Stein (to I.G.), *Ger.* 708,463, June 12, 1941, C.A. 37, 3105 (1943). *French* 853,647, March 23, 1940, C.A. 36, 2565 (1942). {147} Hibbert, Greig, *Can. J. Research* 4, 202 (1931). {148} Sjoberg, *Ber.* 74, 64-65, 69-70 (1941). {149} Braun, *J. Am. Chem. Soc.* 53, 3170 (1930). {150} Lanneweh, *Z. physikal. Chem.* 176, 217 (1928).

{151} Lespiau, *Bull. soc. chim.* (3) 33, 402-463 (1905), *Compt. rend.* 127, 965 (1898), 129, 225 (1899). {152} Hörmann, *Ber.* 12, 23-24 (1879). {153} Ramsaud, *Bull. soc. chim.* (5) 3, 138-139 (1936). {154} I.G., *Brit.* 248,134, June 4, 1931, *Cent.* 1931, II 1193; [C.A. 26, 2748 (1932)]. *French* 702,023, March 27, 1931; *Cent.* 1931, II 1193; C.A. 25, 4012 (1931). {155} Hartenstein, *J. prakt. Chem.* (2) 7, 297-298 (1873). {156} Breslau, *J. prakt. Chem.* (2) 20, 188-193 (1879). {157} de Gegerfelt, *Bull. soc. chim.* (2) 23, 160-161 (1871). {158} Levene, Walti, *J. Biol. Chem.* 79, 363-376 (1928). {159} Thomsen, *Ber.* 11, 2136-2137 (1878). {160} Paterno, Cingolani, *Gazz. chim. ital* 38, 1243-247 (1908).

{161} Johnson, Guest, *Am. Chem. J.* 44, 453, 460 (1910). {162} Bailly, Gaumé, *Compt. rend.* 193, 1932-1934 (1934). {163} Bailly, Gaumé, *Bull. soc. chim.* (4) 39, 1420-1428 (1926). {164} Sjoberg, *Svensk Kem. Tid.* 53, 454-457 (1911). *Cent.* 1912, II 25, C.A. 37, 4363 (1913). {165} Abderhalden, Weill, *Fermentforschung* 4, 84 (1920). {166} Truchot, *Ann.* 138, 297-299 (1866). {167} Whitby, *J. Chem. Soc.* 1926, 1460. {168} Humnicki, *Bull. soc. chim.* (4) 45, 281 (1929). {169} Weinschenk, *Chem. Ztg* 29, 1311 (1905). {170} Grignard, *Bull. soc. chim.* (3) 29, 944, note 2 (1903).

{171} Kling, *Compt. rend.* 137, 756 (1903); *Bull. soc. chim.* (3) 31, 14-16 (1904). {172} Stahl, Cottle, *J. Am. Chem. Soc.* 65, 1782-1783 (1943). {173} Koelsch, McElvann, *J. Am. Chem. Soc.* 52, 1164-1169 (1930). {174} Fournneau, Tiffeneau, *Bull. soc. chim.* (4) 1, 1227-1233 (1907). {175} J. D. Riedel, A.G., *Ger.* 183,361, April 10, 1907, *Cent.* 1907, I 1607, [C.A. 1, 2336 (1907)]. {176} Traube, Lehman, *Ber.* 34, 1972-1980 (1901). {177} Leuchs, *Ber.* 44, 1509-1511 (1911). {178} Michael, Weiner, *J. Am. Chem. Soc.* 58, 1000, 1002 (1936); 56, 2012-2013 (1934). {179} Traube, Lehman, *Ber.* 32, 721 (1899). {180} Haller, *Bull. soc. chim.* (3) 31, 367-369 (1904); (3) 21, 564 (1899).

{181} Stallmann (to du Pont Co.), U.S. 1,977,253, Oct. 16, 1934; *Cent.* 1935, I 2603; C.A. 29, 352 (1935). {182} Stallman (to du Pont Co.), U.S. 1,977,252, Oct. 16, 1934; *Cent.* 1935, I 1620; C.A. 29, 352 (1935). {183} Fauconnier, *Compt. rend.* 106, 605 (1888); 107, 250 (1888). {184} Dains, Brewster, Blair, Thompson, *J. Am. Chem. Soc.* 44, 2641-2642 (1922). {185} Fukagawa, *Ber.* 63, 1344-1346 (1935). {186} Cohn, Friedländer, *Ber.* 37, 3034-3035 (1901). {187} Strukov, *Khim. Farm. Prom.* 1934, No. 2, 11; *Cent.* 1935, I 2806; C.A. 28, 5421 (1934). {188} Fournneau, Ranedo, *Annales soc. espagn. fit. quim.* (2) 18, 133-139 (1920); *Cent.* 1921, III 781; C.A. 15, 1885 (1921). {189} Dreyfus, *French* 702,553, April 11, 1931; *Cent.* 1931, II 2058; C.A. 25, 4284 (1931). {190} Lewis (to Parke-Davis Co.), U.S. 1,664,123, March 27, 1928; *Cent.* 1929, I 1047; C.A. 22, 1593 (1928).

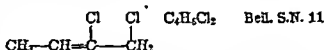
{191} Kolshorn, *Ger.* 346,385, Dec. 29, 1921; *Cent.* 1922, II 574; not in C.A.; *Brit.* 155,575, 155,576, Jan. 13, 1921, *Cent.* 1921, II 691-602; C.A. 15, 1535 (1921); *French* 519,129, June 4, 1921; *Cent.* 1921, IV 803; not in C.A. {192} Knunyantz, *Ber.* 63, 397-399 (1935); *Compt. rend.*

*acad. sci. (U.R.S.S.)* 1935, I 501-506; *Cent.* 1936, II 2915; not in *C.A.* (193) Gerhardt, *Ber.* 24, 352-357 (1891). (194) Baibiano, *Gazz. chim. ital.* 17, 177 (1887); 18, 356-357, 375 (1888); 19, 128 (1889). (195) Rosanov, *J. Russ. Phys.-Chem. Soc.* 48, 1227 (1916); *Cent.* 1923, III 1080; not in *C.A.* (196) Drozdov, Chertuzov, *J. Gen. Chem. (U.S.S.R.)* 4, 969-974 (1934); *Cent.* 1936, I 42; *C.A.* 29, 2148 (1935). (197) Gibson, Harley-Mason, Litherland, Mann, *J. Chem. Soc.* 1942, 172. (198) Eisleb (to I.G.), *Ger.* 473,219, March 13, 1929; *Cent.* 1929, II 350; [*C.A.* 23, 2987 (1929)]; *Brit.* 275,622, Sept. 28, 1927; *Cent.* 1929, II 350; *C.A.* 22, 2171 (1928). (199) Eisleb (to Winthrop Chem. Co.), U.S. 1,645,403, Feb. 16, 1932; *Cent.* 1932, I 3112; *C.A.* 26, 2199 (1932). (200) Ingold, Rothstein, *J. Chem. Soc.* 1931, 1672-1673.

(201) M.L.B., *Ger.* 284,291, May 19, 1915; *Cent.* 1915, I 110; [*C.A.* 10, 94 (1916)]. (202) Reboul, *Compt. rend.* 93, 423 (1881). (203) Schmidt, *Ann.* 337, 116-121 (1904). (204) du Pont Co., *Brit.* 477,981, Feb. 10, 1938; *Cent.* 1938, II 183; not in *C.A.* (205) Tronov, Gershevich, *J. Russ. Phys.-Chem.* 1928, 3389-3390 (1928). (206) Tronov, *J. R. ent.* 1927, II 1145; *C.A.* 22, 2737 (1928). (207) 208) Fromm, *Ann.* 442, 133-134, 142 (1925). (209) Ohle, Haeseler, *Ber.* 69, 2325 (1936). (210) Gabriel, Ohle, *Ber.* 50, 820-821 (1917).

(211) Tomita, *Z. physiol. Chem.* 153, 42-57 (1926). (212) den Otter, *Rec. trav. chim.* 57, 18-20 (1938). (213) Weizmann, Malkowa, *Bull. soc. chim.* (4) 47, 357-358 (1930); *Compt. rend.* 190, 495-496 (1930). (214) Lohmann, *J. prakt. Chem.* (2) 153, 57-64 (1939). (215) Bachman, Mayhew, *J. Org. Chem.* 10, 250, 253 (1945).

**3:5360 1,2-DICHLOROBUTENE-2**  
(low-boilg. stereoisomer)



B.P. 116-118° at 765 mm. (2)

111.5-112.5° at 742 mm. (1)

$D_4^{20} = 1.1544$  (2)  $n_D^{20} = 1.4642$  (2)

$D_4^{18} = 1.1550$  (2)  $n_D^{18} = 1.4576$  (2)

$D_4^{16} = 1.1488$  (1)  $n_D^{16} = 1.45513$  (1)

[See also high-boilg. stereoisomer (3:5615).]

[For prepn. of  $\bar{C}$  (together with its stereoisomer (3:5615)) from 1,2,3-trichlorobutane (3:5935) with KOH at 150° (2), or from 2,2-dichlorobutane (3:7415) or 2,3-dichlorobutane (3:7615) with alc. KOH (5), see indic. refs.; for formn. of  $\bar{C}$  (together with its stereoisomer and also 2,4-dichlorobutene-2 (3:5550)) from 2-chlorobutene-2 (3:7105) by actn. of  $\text{Cl}_2$  at 350° see (3).]

$\bar{C}$  with 1 mole  $\text{Cl}_2$  + 1.5 moles  $\text{NaHCO}_3$  at 0° gives (100% yield (4)) 1,2,2,3-tetrachlorobutane (3:9078).

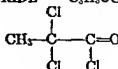
$\bar{C}$  on hydrolysis by htg. with 2 pts. aq. + 1 mole powdered  $\text{CaCO}_3$  at 70° for 4 hrs. gives (1) a mixt. of about equal parts of 2-chlorobuten-2-ol-1 (3:8240) and (by allylic transposition) 3-chlorobuten-3-ol-2 (3:9115).

$\bar{C}$  on oxidn. with  $\text{KMnO}_4$  in acetone gives (1) chloroacetic acid (3:1370) +  $\text{AcOH}$  (1:1010) +  $\text{HCl}$ . —  $\bar{C}$  in  $\text{CCl}_4$  at -17° treated with  $\text{O}_2$  followed by aq. gives acetaldehyde (1:0100).

**3:5360** (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 7, 658-662 (1937); *Cent.* 1937, II 371; *C.A.* 31, 5754 (1937). (2) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 6, 1553-1555 (1936); *Cent.* 1937, I 3786; *C.A.* 31, 2165 (1937). (3) N. V. Bataafsche Petroleum Maatschappij, *Brit.* 468,016, July 22, 1937; French 810,112, March 15, 1937; *Cent.* 1937, II 4102. (4) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, II 4222; *C.A.* 33, 4190 (1939). (5) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 7, 663-666 (1937); *Cent.* 1937, II 371; *C.A.* 31, 5754 (1937).

3:5372  $\alpha,\alpha$ -DICHLOROPROPIONYL CHLORIDE  $C_3H_3OCl_3$ 

Beil. II - 251

 $\Pi_1$ —  
 $\Pi_2$ -(228)

B.P. 117.4–117.8° at 763 mm. (1)

 $D_4^{20} = 1.4062$  (1)  $n_D^{20} = 1.45240$  (1)

110–115° (2)

68–73° at 88–90 mm. (3)

Colorless lachrymatory liq. with penetrating odor.

[For prepn. of  $\bar{C}$  from  $\alpha,\alpha$ -dichloropropionic acid (3:6162) with  $\text{SOCl}_2$  under reflux for 10 hrs. (1) or with  $\text{PCl}_3$  (2) see indic. refs., from pyruvic acid ( $\text{CH}_3\text{CO}\cdot\text{COOH}$ ) (1:1040) with  $\text{PCl}_3$  see (2) (4).]

[For study of rate of reaction of  $\bar{C}$  in dioxane with  $\beta$ -chloroethanol (3:5552) see (1)]

$\bar{C}$  with aq. readily hydrolyzes to  $\alpha,\alpha$ -dichloropropionic acid (3:6162) q.v.

①  $\alpha,\alpha$ -Dichloropropionamide: lfts. from dil. alc., m.p. 117–118° (3) (5), 116–117° (2), 116° (4) [From  $\bar{C}$  with conc. aq.  $\text{NH}_4\text{OH}$  (2); for other ways see under  $\alpha,\alpha$ -dichloropropionic acid (3:6162).]

②  $\alpha,\alpha$ -Dichloropropion-*N*-ethylamide: m.p. 51–52° (3). [From  $\bar{C}$  with  $\text{EtNH}_2$  (3).]

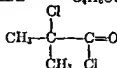
—  $\alpha,\alpha$ -Dichloropropionanilide: m.p. 101° (3). [Reported only by indirect means (3).]

—  $\alpha,\alpha$ -Dichloropropion-*p*-toluidide: m.p. 84–86° (6). [Reported only by indirect means (6).]

3:5372 (1) Leimu, *Ber.* 70, 1046, 1050 (1937). (2) Beckurts, Otto, *Ber.* 11, 386–391 (1878). (3) von Braun, Jostes, *Münch. Ann.* 453, 126, 135 (1927). (4) Klimentko, *Ber.* 3, 465–468 (1870). (5) Otto, *Ann.* 132, 183 (1864). (6) Bischoff, Walden, *Ann.* 279, 93 (1894).

3:5385  $\alpha$ -CHLORO-ISOBUTYRYL CHLORIDE $C_4H_7OCl_2$ 

Beil. II - 295

 $\Pi_1$ —  
 $\Pi_2$ -(263)

B.P. 117–118° (1)

 $n_D^{20} = 1.4369$  (1)

113–114° (2)

The h.p. of 125–126° given by (3) is incorrect (1).

[For prepn. of  $\bar{C}$  from isobutyryl chloride (3:7270) with  $\text{Cl}_2$  (3) (4) (5) or with  $\text{SO}_2\text{Cl}_2$  + dihenzoyl peroxide in  $\text{CCl}_4$  (20%  $\bar{C}$  + 80%  $\beta$ -chloro isomer (1)) see indic. refs.; for prepn. of  $\bar{C}$  from  $\alpha$ -hydroxyisobutyric acid (1:0431) with  $\text{SOCl}_2$  (together with other products) see (2)]

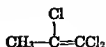
[For reactn. of  $\bar{C}$  with  $\text{MeOH}$  yielding methyl  $\alpha$ -chloro-isobutyrate (3:7918) see (5).]

$\bar{C}$  on hydrolysis with aq. yields  $\alpha$ -chloro-isobutyric acid (3:0235) q.v.

3:5385 (1) Kharasch, Brown, *J. Am. Chem. Soc.* 62, 925–929 (1940). (2) Blaise, Montagne, *Compt. rend.* 174, 1555 (1922). (3) Michael, Garner, *Ber.* 34, 4054–4055 (1901). (4) Henry, *Compt. rend.* 142, 1024 (1906); *Bull. acad. roy Belg* 1906, 206–226; *Cent.* 1906, II 227. (5) du Pont Co. & Loder, *Brit.* 428,223, May 9, 1935; *Cent.* 1936, I 179; *C.A.* 29, 6607 (1935).



## 3:5395 1,1,2-TRICHLOROPROPENE-1

 $\text{C}_3\text{H}_3\text{Cl}_3$ 

Beil. I - 200

I<sub>1</sub>-  
I<sub>2</sub>-

B.P. 118° (1)

116-117° (2)

115° (3)

 $D_4^{15} = 1.387$  (3)

[For prepn. of  $\bar{\text{C}}$  from 1,1,1,2-tetrachloropropane (3:5785) in 93% yield by htg. with aq. or alc. alk. for 3 hrs. at 95° see (1); for prepn. of  $\bar{\text{C}}$  from 1,1,2,2-tetrachloropropane (3:5825) with alc. KOH or alc.  $\text{NH}_4\text{OH}$  see (2) (3).]

[For use of  $\bar{\text{C}}$  as dry cleaner and spot remover (4) or in degreasing of metals (5); for use in dewaxing of mineral oils see (6).]

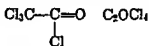
$\bar{\text{C}}$  with  $\text{Cl}_2$  yields (3) 1,1,1,2,3-pentachloropropane (3:4740), m.p. 179°.

it. 469,051, July 19, 1937; *Cent.* 1938, I 1218; *C.A.* 32, 596  
18, 2668 (1895). (3) Borsche, Fittig, *Ann.* 133, 117-119

U.S. 2,116,437, May 3, 1938; *Cent.* 1938, II 796; *C.A.* 32,

1938, 4936 (1938). (6) Standard Oil Development Co., French 790,852, Nov. 28, 1935;  
*Cent.* 1936, I 2672; *C.A.* 30, 3323 (1936).

## 3:5420 TRICHLOROACETYL CHLORIDE

 $\text{C}_2\text{OCl}_4$ 

Beil. II - 210

II<sub>1</sub>-( 94)II<sub>2</sub>-(200)

B.P. 118° cor.

(1) (8)

 $D_4^{20} = 1.6202$  (3);  $n_D^{20} = 1.4701$  (5);

117-118°

at 760 mm. (2)

1.6179 (5)

1.46949 (3)

117.9°

at 754 mm. (3)

116.3-118.5°

(4)

116.4°

at 755 mm. (5)

116-117°

at 726 mm. (6)

[For prepn. of  $\bar{\text{C}}$  from trichloroacetic acid (3:1150) with  $\text{PCl}_3$  (1) (7) (8), with  $\text{PCl}_3$  +  $\text{ZnCl}_2$  (25% yield (9)), with  $\text{SOCl}_2$  (yield: 12% (9), 30% (23)) in  $\text{C}_6\text{H}_6$  (60% yield (3)) or in pyridine (90% yield (10)), with  $\text{P}_2\text{O}_5$  +  $\text{HCl}$  gas (11), with benzotrichloride (3:6540) +  $\text{ZnCl}_2$  at 100° (77% yield (12)), with benzoyl chloride (3:6240) (51-56% yield (13)) see indic. refs.]

[For formn. of  $\bar{\text{C}}$  from trichloroacetic acid at 300° (together with  $\text{CO}$ ,  $\text{CO}_2$  +  $\text{HCl}$ ) see (14); from acetyl chloride (3:7065) with 3 moles  $\text{PCl}_5$  see (11); from hexachloroethane (3:4835) with  $\text{SO}_2$  at 150° see (15); from pentachloroethane (3:5880) or *sym.*-tetrachloroethane (3:5750) in ultra-violet light and  $\text{O}_2$  see (16); from tetrachloroethylene (3:5460) with  $\text{SO}_3$  (15), with  $\text{H}_2\text{SO}_4$  +  $\text{HNO}_3$  (together with other products) (17), with ozone (18) (19), with oxygen in pres. of  $\text{Br}_2$  or conc.  $\text{HNO}_3$  (20), with oxygen by chlorine sensitized photo-oxidation (21) cf. (30) (31), or with oxygen in ultra-violet light (16) see indic. refs.; from diethyl ether on protracted chlorination in sunlight, from decachlorodiethyl ether (3:1676) on distn. see (22), or from distn. of pentachloroethyl trichloroacetate see (22), from  $\text{CCl}_4$  (3:5100) +  $\text{AlCl}_3$  +  $\text{CO}$  gas at 200° and 250 atm. (37% yield) see (32).]

[ $\bar{\text{C}}$  on htg. (13) or on htg. with  $\text{AlCl}_3$  (23) yields carbon tetrachloride (3:5100) +  $\text{CO}$ ;  $\bar{\text{C}}$  on htg. at 600° yields (24) carbon tetrachloride (3:5100) + hexachloroethane (3:4835) +  $\text{CO}$  + phosgene (3:5000).]

[ $\bar{\text{C}}$  on treatment at -5° with dry  $\text{HBr}$  gas gives (70% yield (24)) trichloroacetyl bromide, b.p. 143°;  $\bar{\text{C}}$  similarly treated with dry  $\text{HI}$  gas gives (71.5% yield (6)) trichloroacetyl iodide, b.p. 74-74.2° at 30 mm. (6).]

$\bar{C}$  with MeOH should yield readily methyl trichloroacetate (3:5800), b.p. 153.8°;  $\bar{C}$  with EtOH yields (1) ethyl trichloroacetate (3:5950), b.p. 168°. (For study of rate of reactn. see (2).)

$\bar{C}$  with pure freshly distilled  $AlCl_3 + C_6H_6$  yields (25) (26) triphenylvinyl alcohol ( $\omega, \omega$ -diphenylacetophenone) [Beil. VII-522, VII<sub>1</sub>-(291)], m.p. 137°; with moist  $AlCl_3 + C_6H_6$ , however,  $\bar{C}$  gives instead (25) (27) (28)  $\omega, \omega, \omega$ -trichloroacetophenone (3:6874), b.p. 256-257° (25). —  $\bar{C}$  with  $Me_2Zn$  yields (29) pentamethylethyl alcohol [Beil. I-418, I<sub>1</sub>-(207), I<sub>2</sub>-(447)]. —  $\bar{C}$  with  $EtMgBr$  in ether at 10° gives (33) 1,1,1-trichlorobutanol-2 (3:5955).

$\bar{C}$  hydrolyzes readily with aq. yielding trichloroacetic acid (3:1150); for the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see trichloroacetic acid (3:1150).

3:5420 (1) Gal, *Bull. soc. chim.* (2) 20, 11-13 (1873). (2) Branch, Nixon, *J. Am. Chem. Soc.* 58, 2499-2504 (1936). (3) Leimu, *Ber.* 70, 1049 (1937). (4) Cheng, *Z. physik. Chem.* B-26, 295 (1934). (5) Martin, Partington, *J. Chem. Soc.* 1936, 162. (6) Gustus, Stevens, *J. Am. Chem. Soc.* 55, 376 (1933). (7) Delacre, *Bull. acad. roy. Belg.* 1902, 189-202, *Cent.* 1902, I 1197. (8) Thorpe, *J. Chem. Soc.* 37, 189-190 (1880). (9) Clark, Bell, *Trans. Roy. Soc. Can.* (3) 27, III 97-103 (1933). (10) Carré, Liebermann, *Compt. rend.* 199, 1422-1423 (1934).

(11) Friederici, *Ber.* 11, 1971 (1878). (12) Rabcewicz-Zubkowski, *Roczniki Chem.* 9, 528 (1929); *Cent.* 1929, II 2767; *C.A.* 24, 61 (1930). (13) Brown, *J. Am. Chem. Soc.* 60, 1325-1328 (1938). (14) Engler, Steude, *Ber.* 26, 1443-1444 (1893). (15) Prud'homme, *Compt. rend.* 70, 1138 (1870). (16) Müller, Ehrmann, *Ber.* 69, 2207-2210 (1936). (17) Biltz, *Ber.* 35, 1535-1536 (1902). (18) Besson, *Compt. rend.* 118, 1348 (1894); 121, 125 (1895). (19) Swarts, *Bull. acad. roy. Belg.* (3) 30, 532-552 (1898); *Cent.* 1898, I 588-589. (20) Consortium für Elektrochem. Ind., *Ger.* 840,872, Sept. 19, 1921; *Cent.* 1921, IV 1101.

(21) Dickinson, Carrico, *J. Am. Chem. Soc.* 56, 1473-1480 (1934). (22) Malaguti, *Ann. chim.* (8) 16, 5-28, 64 (1846). (23) Böeseken, *Rec. trav. chim.* 29, 100, 112 (1910). (24) Simons, Sloat, Meunier, *J. Am. Chem. Soc.* 61, 435-436 (1939). (25) Biltz, *J. prakt. Chem.* (2) 142, 196-197 (1935). (26) Biltz, *Ber.* 32, 654-655 (1899). (27) Staudinger, *Kon. Ann.* 384, 112 (1911). (28) Gautier, *Ann. chim.* (6) 14, 398-402 (1888). (29) Bogomolez, *Ann.* 209, 78-82 (1881). (30) Schott, Schumacher, *Z. physik. Chem.* B-49, 107-125 (1941); *Cent.* 1941, II 2549; *C.A.* 38, 3551 (1944).

(31) Kirkbride (to Imperial Chem. Ind., Ltd.), U.S. 2,321,823, June 15, 1943; *C.A.* 37, 6676 (1943); *B.* 37, 4746. (1945). *C.A.* 4085

3:5425 1-CHLOROPROPANONE-2  $CH_3-C(=O)-CH_2Cl$   $C_3H_5OCl$  Beil. I - 653  
(Chloroacetone; acetyl chloride)  $\begin{array}{c} O \\ || \\ Cl \end{array}$  I<sub>1</sub>-(344)  
chloride) I<sub>2</sub>-(718)

B.P.	B.P. (cont'd)	
119-120° (1) (20)	60-62° at 50 mm. (10)	$D_4^{25} = 1.123$ (189)
119.7° at 760 mm. (2)	46° at 46 mm. (3)	$D_4^{20} = 1.170$ (11)
119.5° (3)	35° at 29 mm. (6)	$D_{16}^{17} = 1.164$ (12)
119.3° (4)	20° at 12 mm. (6)	
118.8-119.4° (5)		$D_{16}^{16} = 1.162$ (7) cf. (189)
119° at 760 mm. (6)		
119° at 735 mm. (7)		$D_{13}^{13} = 1.158$ (9) cf. (189)
118° at 723 mm. (8)		
117-118° (9)		$D_4^{15} = 1.135$ (189)

$\bar{C}$  when pure is colorless liq. —  $\bar{C}$  turns dark on exposure to light. —  $\bar{C}$  on long exposure to light, acids, or metals resinifies to a dark mass, m.p. above 350°, which fumes in air and dis. in fumg.  $HNO_3$ , but does not react with fumg.  $H_2SO_4$ ,  $NH_2OH$ , or phenylhydrazine

nor hydrolyze with 50% KOH (13). — [For stabilization of  $\bar{C}$  by means of addn. of 1%  $\text{CaCO}_3$  (14) or 0.1% aq. (15) see indic. refs.]

$\bar{C}$  is sol. in 10 pts. aq. (7) but does not form crystn. hydrates with it (9) (for prepn. of anhydrous  $\bar{C}$  using  $\text{CaSO}_4$  see (16));  $\bar{C}$  is volatile with steam (9); sol. in alc., ether,  $\text{CHCl}_3$ .

$\bar{C}$  has very pronounced lachrymatory properties; for studies of this property see (17) (18).

$\bar{C}$  forms azeotropes with several org. liqs. (19); e.g.,  $\bar{C}$  with toluene (1:7405) forms a const.-boilg. mixt., h.p. 109.2° at 760 mm., contg. 28.5%  $\bar{C}$ ;  $\bar{C}$  with isohutyl alc. (1:6165) forms a const.-boilg. mixt., b.p. 105.8° at 760 mm., contg. 36%  $\bar{C}$ ;  $\bar{C}$  with ethyl *n*-butyrate (1:3127) forms a const.-boilg. mixt., h.p. 117.2° at 760 mm., contg. 53%  $\bar{C}$ ;  $\bar{C}$  with isohutyl acetate (1:3115) forms a const.-boilg. mixt., h.p. 116.7°, contg. 30%  $\bar{C}$ .

[For prepn. of  $\bar{C}$  from acetone (1:5400) with  $\text{Cl}_2$  (188) (9) (20) (21) (22) (23) (24) (25) (yield is poor and contaminated with higher chlorination prods. especially 1,1-dichloropropanone-2 (*unsym.*-dichloroacetone) (3:5430) whose b.p. is very close to that of  $\bar{C}$ ); with  $\text{Cl}_2$  in pres. of  $\text{CaCO}_3$  (yield 82% (3)) (26) (27) (28); with  $\text{Cl}_2$  in vapor-phase chlorination (29) (30) (21) in pres. of  $\text{NiCl}_2$  (38); by electrolysis in  $\text{HCl}$  (97% yield (32)) (36) using Pt electrodes (with graphite or lead electrodes resultant  $\bar{C}$  is reduced) even using alternating current (35% yield (33)); with  $\text{Cl}_2\text{O}$  (34); with  $\text{HOCl}$  (22) (27) (35); with  $\text{EtOCl}$  (3:7022) (1); with *N*-chlorourea in aq. soln. (37); or with  $\text{SO}_2\text{Cl}_2$  (72% yield (189)) see indic. refs.]

[For prepn. of  $\bar{C}$  from acetone (1:5400) with benzenediazonium chloride (solid) in pres. of  $\text{CaCO}_3$  (39) (40), or with aq. solns. of other diazonium chlorides (especially those with negative substituents such as those from *p*-nitroaniline, *p*-chloroaniline, or 2,4-dichloroaniline) in pres. of  $\text{CuCl}_2 + \text{NaOAc}$  (41), see indic. refs.]

[For prepn. of  $\bar{C}$  from 1-chloropropanol-2 (propylene  $\alpha$ -chlorohydrin) (3:7747) by oxidn. with  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$  (42) (43) (44) (45),  $\text{CrO}_3 + \text{dil. H}_2\text{SO}_4$  (43),  $\text{CrO}_3/\text{AcOH}$  (43),  $\text{HNO}_3$  (43) (44) (45),  $\text{HOCl}$  (42), or  $\text{Ca}(\text{OCl})_2$  (46) see indic. refs.; from 3-chloro-2-methylpropene-1 (methallylchloride) (3:7145) (10), or from 1-chloro-2-methylbutene-2 (3:7485) (47), or from 1,3-dichloro-2-methylpropene-1 (3:5590) (48), or from 1,4-dichloro-2-methylbutene-2 (3:9204) (49) with  $\text{O}_3$  see indic. refs.]

[For prepn. of  $\bar{C}$  from ethyl  $\gamma$ -chloroacetoacetate (3:6375) (50) or from  $\alpha$ -chloroacetoacetanilide (51) by hydrolytic cleavage with  $\text{HCl}$  see indic. refs.; from 1,3-dichloropropene-2 (3:5280) by soln. in conc.  $\text{H}_2\text{SO}_4$  and distn. with aq. see (52); from allyl chloride (3:7035) with  $\text{HgO} + \text{HOCl}$  see (53); from 1,2-epoxypropane (propylene oxide) (1:6115) with  $\text{Cl}_2$  at 0° see (54); from diketene +  $\text{Cl}_2$  in cold followed by treatment with aq. see (55).]

[For use of  $\bar{C}$  in refining of mineral oils see (56); in prepn. of photosensitizing cyanine dyes see (57).]

Pyrolysis. [ $\bar{C}$  passed through tube at 450° pyrolyzes into acetaldehyde (1:0100), acetone (1:5400), crotonaldehyde (1:0150) +  $\text{HCl}$  (58).]

Reduction. [ $\bar{C}$  on reduction with  $\text{Zn} + \text{HCl}$  (7) or on electrolysis in  $\text{HCl}$  soln. using graphite or lead electrodes (32) yields acetone (1:5400);  $\bar{C}$  on reduction with  $\text{AlEt}_3$  etherate as directed (59) gives (70% yield) 1-chloropropanol-2 (3:7747), b.p. 78–81° at 80 mm. (59);  $\bar{C}$  on phytochemical reduction using yeast (60) gives (25% yield) 1-chloropropanol-2 (3:7747); for polarographic study of oxidn.-reductn. potential of  $\bar{C}$  see (61).]

Oxidation.  $\bar{C}$  on oxidn. with  $\text{KMnO}_4$  (49) (62),  $\text{HNO}_3$ ,  $\text{CrO}_3$ , etc. (62), yields chloroacetic acid (3:1370) and  $\text{AcOH}$  (1:1010). —  $\bar{C}$  with moist silver oxide yields (7) glycolic acid (1:0430), acetic acid (1:1010), and formic acid (1:1005).

Halogenation. [ $\bar{C}$  with  $\text{Cl}_2$  even in cold gives (26) more highly chlorinated acetones; e.g.,  $\bar{C}$  with  $\text{Cl}_2$  at 30–40° yields (63) 1,1,3-trichloropropanone-2 (3:5957) and 1,1,1-trichloropropanone-2 (3:5620);  $\bar{C}$  with  $\text{Cl}_2$  at 50–70° yields (63) cf. (64) *sym.*-tetrachloro-

acetone (3:6050), *unsym.*-tetrachloroacetone (3:6085), and pentachloroacetone (3:6205);  $\bar{C}$  with  $Cl_2$  at 50–100° in light (63) (65) or under press. (66) yields hexachloroacetone (3:6312). — Note that  $\bar{C}$  with  $Ca(OCl)_2$  undergoes both chlorination and subsequent cleavage yielding (46)  $CHCl_3$  (3:5050).]

[ $\bar{C}$  with  $Br_2$  (3 moles) at 100° yields (67) 3,3,3-tribromo-1-chloropropanone-2 [Beil. I-658], b.p. 215°, 13.0° at 25 mm.]

Reactions of the halogen atom of  $\bar{C}$  (see also further below under formn. of heterocyclic systems).  $\bar{C}$  with excess aq. alkali presumably yields propanone-2-ol-1 (acetol) (1:5455) and therefore reduces Fehling's soln.; the halogen atom of  $\bar{C}$  is so reactive that  $\bar{C}$  slowly neutralizes 1 equiv. alk. (68);  $\bar{C}$  with  $NaOEt$  in abs. alc. yields acetol ethyl ether (ethoxyacetone) [Beil. I-822, I<sub>1</sub>-(418), I<sub>2</sub>-(867)], h.p. 128° at 760 mm. (for study of rate of reaction see (69)).

[ $\bar{C}$  with phenol (1:1420) + anhydrous  $K_2CO_3$  in acetone stirred 24 hrs. at room temp. or refluxed 3 hrs. (70) (note that in pres of  $KI$  yield jumps to 92.5% (191)), or  $\bar{C}$  with sodium phenolate in phenol (71) (72) or in toluene (73), gives (yields: 21–23% (70), 16% (73)) phenoxyacetone (1:5534), b.p. 117–124° at 19 mm. (70) (note that  $\bar{C}$  + phenol + aq.  $NaOH$  gives only black resin (73)) (for application of this type of reactn. to other monohydric phenols such as tetralol-2 (5,6,7,8-tetrahydronaphthol-2) (74) (75) or *p*-*tert*-butylphenol (1:1510) (75) or  $\beta$ -naphthol (1:1540) (191) see indic. refs.). — Note that  $\bar{C}$  with phenol (3 moles) + fuming  $HCl$  at 100° reacts in a dif. sense to give (50% yield (76)) a *tris*-(hydroxyphenyl)propane of undetd. struct.; for formn. of resins from  $\bar{C}$  + phenol see (77) (78).]

[ $\bar{C}$  with  $KI$  in aq.  $MeOH$  (79) (80) or in acetone (5) gives (75% yield (80)) iodoacetone [Beil. I-660, I<sub>1</sub>-(345), I<sub>2</sub>-(719)], oil, b.p. 58.4° at 11 mm. (79) (oxime, pr. from pet. eth., m.p. 64.5° (79)); for study of rate of this reactn. in acetone at 0° and 10° see (5). —  $\bar{C}$  with  $K_2SO_3$  (or  $Na_2SO_3$ ) yields (81) salts of acetonesulfonic acid [Beil. IV-19, IV<sub>2</sub>-(530)]. — For study of rate of reactn. of  $\bar{C}$  with aq.  $Na_2S_2O_3$  see (82). —  $\bar{C}$  with  $Na_2S$  in acetone yields (83) (84) *bis*-(acetylonyl) sulfide, m.p. 49° (83), b.p. 126° at 14 mm. (83), 125° at 18 mm. (84) (earlier work (85) using alc. as solvent could not be checked (83) (84).)]

[ $\bar{C}$  with aq.  $NaSCN$  stirred 10 hrs. at 25° (86), or  $\bar{C}$  with  $Ba(SCN)_2$  directly (87) or in alc. (88) (89) cf. (90), gives (95% yield (86)) thiocyanacetone (acetylonyl thiocyanate) [Beil. III-179, III<sub>1</sub>-(72), III<sub>2</sub>-(125)], oil, b.p. 73.5–74.5° at 1 mm. (86),  $D_4^{25} = 1.1892$  (86) (for use of this prod. as anti-oxidant for rubber (91), as stabilizer for cellulose (92), or as 1% soln. in petroleum as insecticide (93) see indic. refs.); note that thiocyanacetone, although insensitive to dil. aq.  $HCl$  (87), with  $HCl$  gas in cold (86) or conc.  $HCl$  on boilg (89) adds 1 mole  $HCl$  and ring-closes to 2-chloro-4-methylthiazole, oil, b.p. 167–167.5° at 754 4 mm., 69° at 14 mm. (86); note also that thiocyanacetone with aq.  $NaHCO_3$  (94) (or  $\bar{C}$  + aq.  $KSCN$  +  $NaHCO_3$  (86)) yields 2-hydroxy-4-methylthiazole (4-methylthiazolone-2) ("α-methylrhodime") [Beil. XXVII-158, XXVII<sub>1</sub>-(264)], ndls. from aq. or ether, m.p. 105–106° (94), 102–103° (86).]

[ $\bar{C}$  with  $Na$  salts of sulfonic acids gives the corresp. alkyl- (or aryl)sulfonylacetones: e.g.,  $\bar{C}$  with  $Na$  methanesulfinate gives (95) methanesulfonylacetone, m.p. 54° (95) (96);  $\bar{C}$  with  $Na$  benzenesulfinate in alc. gives on refluxing (95% yield (97)) benzenesulfonylacetone [Beil. VI-307, VI<sub>1</sub>-(145)], lfts. from alc., m.p. 57° (97);  $\bar{C}$  with  $Na$  *p*-toluenesulfinate yields (97) *p*-toluenesulfonylacetone [Beil. VI-421, VI<sub>1</sub>-(210)], m.p. 51° (97) (98); many other analogous cases are known.]

[ $\bar{C}$  with tertiary amines gives the corresp. quaternary ammonium chloride salts: e.g.,  $\bar{C}$  with dry  $Me_3N$  in abs. ether (99) or abs. alc. (100) (101) yields trimethyl-acetylonyl-ammonium chloride [Beil. IV-315, IV<sub>2</sub>-(763)], very hygroscopic white solid;  $\bar{C}$  with pyridine gives corresp. salt (for study of rate in abs. alc. at 55.6° see (102)). —  $\bar{C}$  with triphenyl-

phosphine in  $C_6H_6$  at  $75-80^\circ$  for 15 hrs. yields (103) triphenyl-acetonyl-phosphonium chloride, m.p.  $234^\circ$  dec. (103). —  $\bar{C}$  with hexamethylenetetramine in  $CHCl_3$  grad. ppts. an addn. prod. (poor yield (104)), ndls., m.p.  $122^\circ$  (104).]

[ $\bar{C}$  with dry  $NH_3$  may yield (9) a little aminoacetone (acetonylamine) [Beil. IV-314, IV<sub>1</sub>-(450), IV<sub>2</sub>-(763)], but the reactn. is unsatisfactory and other methods (105) are preferred for prepn. of the latter;  $\bar{C}$  (in excess) with aq. soln. (30%) of  $Me_2NH$  yields (106) dimethylaminoacetone [Beil. IV-314], misc. with aq., alc., ether, b.p.  $123^\circ$  (106);  $\bar{C}$  (1 mole) with  $Et_2NH$  (2 moles) in ether yields (106) diethylaminoacetone [Beil. IV-316], h.p.  $155-156^\circ$  (106). — Many analogous cases are recorded.]

Reactions of  $\bar{C}$  involving the H atoms of its  $-CH_2Cl$  grouping.  $\bar{C}$  with salicylaldehyde (1:0205) in alc. KOH refluxed for 15 min. (107) (108), or in alc. NaOH refluxed 2 hrs. (109), or  $\bar{C}$  + Na salt of salicylaldehyde in dry  $C_6H_6$  under reflux (110), gives (yields: 60-85% (107), 75% (109), 60% (108)) 2-(acetyl)coumarone (2-acetobenzofuran) [Beil. XVII-338], colorless lfts. from alc., m.p.  $76^\circ$  (107),  $75-76^\circ$  (109),  $74-75^\circ$  (108) (110) (corresp. oxime, ndls. from dil. alc., m.p.  $150^\circ$  (111), phenylhydrazone, cryst. from alc., m.p.  $153-154^\circ$  (107), semicarbazone, ndls. from dil. alc., m.p.  $217^\circ$  (107)). —  $\bar{C}$  with *p*-dimethylaminobenzaldehyde in AcOH with HCl gas yields (112)  $\alpha$ -chloro- $\alpha$ -(*p*-dimethylaminobenzal)acetone, yel. lfts. from alc., m.p.  $115^\circ$  (112) (corresp. phenylhydrazone, m.p.  $206-208^\circ$  (112), semicarbazone, m.p.  $202-203^\circ$  (112)), accompanied by a little  $\alpha$ -chloro- $\alpha'$ -bis-(*p*-dimethylaminobenzal)acetone, cryst. from 1:1 abs. alc. +  $C_6H_6$ , m.p.  $225^\circ$  (112). —  $\bar{C}$  with diazotized aniline in pres. of NaOAc at  $0^\circ$  yields (113) (49) cf. (114) 1-(benzeneazo)-1-chloroacetone [Beil. XV-342], yel. ndls. from boilg. alc., m.p.  $136-137^\circ$  (113),  $135-136^\circ$  (49).

Reactions of  $\bar{C}$  involving the keto group.  $\bar{C}$  with satd. aq.  $NaHSO_3$  soln. yields (51) a crystn.  $NaHSO_3$  cpd. cf. (7).

[ $\bar{C}$  with HCN as directed gives (yields: 94% (119), 87-90% (192)) (21) (115) (116)  $\beta$ -chloro- $\alpha$ -hydroxyisobutyronitrile (chloroacetone cyanohydrin) [Beil. III-317], oil, b.p.  $110^\circ$  at 22 mm. (117)  $108-110^\circ$  at 20 mm. (192),  $103-104^\circ$  at 16 mm. (115),  $D_4^{25} = 1.2027$  (117),  $n_D^{20} = 1.4520$  (192),  $n_D^{15} = 1.45362$  (117); this prod. on distillation at ord. press. or even on stdg. in the air readily dissociates into the original components; on saponification with HCl, however, it gives (62% yield (192)) (5) (115)  $\beta$ -chloro- $\alpha$ -hydroxyisobutyric acid [Beil. III-317, III<sub>1</sub>-(120), III<sub>2</sub>-(224)], ndls. from  $C_6H_6$ , m.p.  $110^\circ$  (118)  $109-110^\circ$  (192). —  $\bar{C}$  (1 mole) with aq. KCN (1 mole) gives 43% yield (119) of a cpd.,  $C_3H_5O_2N_2$ , m.p.  $183^\circ$ , formerly supposed to be  $\alpha$ -aceto- $\beta$ -hydroxy- $\beta$ -methylglutaro(di)nitrile [Beil. III-883] but now (119) regarded as 2,4-dicyano-2,5-dimethyl-5-hydroxytetrahydrofuran (for mechanism of its formn. and review of earlier literature see (119)).]

[ $\bar{C}$  forms acetals or similar cpds.: e.g.,  $\bar{C}$  with triethyl orthoformate (1:3241) in EtOH + a drop of  $H_2SO_4$  gives (yields: 90% (120), 87% (80)) cf. (190) chloroacetone diethylacetal [Beil. I-654, I<sub>2</sub>-(718)], h.p.  $161-162^\circ$  u.c. (120)  $81-82^\circ$  at 50 mm. (190),  $52-53^\circ$  at 14 mm. (80),  $D_4^{25} = 1.002$  (120); for acetals from  $\bar{C}$  with glycerol (1:6540) (121) or pyrocatechol (1:1520) (122) see indic. refs.]

[ $\bar{C}$  with phenyl isocyanide + AcOH in ether gives (123)  $\alpha$ -acetoxy- $\beta$ -chloroisobutyranilide;  $\bar{C}$  with phenyl isocyanide + BzOH in ether gives (123)  $\alpha$ -benzoyloxy- $\beta$ -chloro-isobutyranilide.]

[ $\bar{C}$  with  $RMgX$  cpds. (1 mole) in ether in general reacts normally with the ketonic group to give addn. prods. which with aq. yields the corresp. tertiary alcs.: e.g.,  $\bar{C}$  with  $MeMgBr$  gives (38% yield (124)) (125) 1-chloro-2-methylpropanol-2 ( $\alpha$ -isobutylene chlorohydrin) (3:7752) (accompanied as a result of reactn. of a second  $MeMgBr$  and rearr. (126) (127) by some 2-methylbutanol-2 (1:6160)); for corresp. reactn. of  $\bar{C}$  with  $EtMgBr$  yielding

1-chloro-2-methylbutanol-2 (3:8175) see (123); for corresp. reacta. of  $\bar{C}$  with  $n\text{-C}_4\text{H}_9\text{MgBr}$ ,  $n\text{-C}_4\text{H}_9\text{MgBr}$ ,  $\text{iso-C}_4\text{H}_9\text{MgBr}$ ,  $\text{iso-C}_5\text{H}_{11}\text{MgBr}$ ,  $n\text{-C}_6\text{H}_{13}\text{MgBr}$ , and  $n\text{-C}_7\text{H}_{15}\text{MgBr}$  see (129); for corresp. reacta. of  $\bar{C}$  with *tert*-butylethynyl  $\text{MgBr}$  (130), with *n*-amylethynyl  $\text{MgBr}$  (131), or with ethynyl  $\text{bis-MgBr}$  (132) see iadic. refs. —  $\bar{C}$  with  $\text{C}_6\text{H}_5\text{MgBr}$  yields (133) 1-chloro-2-phenylpropanol-2 [Beil. VI-507]; note, however, that if the initial addn. cpd. is htd. at 130–140° prior to hydrolysis rearr. occurs and the prod. then (134) is phenylacetone (1:5118). — For reacta. of  $\bar{C}$  with *o*-xetyl  $\text{MgI}$  see (70).]

[ $\bar{C}$  with abs. diazomethane (free from  $\text{MeOH}$ ) in dry ether yields (135) 1-chloro-2-methyl-2,3-epoxybutane, b.p. 124° (135).]

Condensation reactions of  $\bar{C}$  (usually yielding heterocyclic compounds). [ $\bar{C}$  with acetaldehyde (1:0100) +  $\text{NH}_4\text{OH}$  in pres. of  $\text{Cu}(\text{OAc})_2$  gives (49% yield (136)) 2,4-(or 5)-dimethylimidazole [Beil. XXIII-79, XXIII-(25)], b.p. 266° at 733 mm., m.p. 92° (136) ( $\bar{B}.\text{HCl}$ , m.p. 205,  $\bar{B}.\text{PhOH}$ , m.p. 142–143° (136)).]

[ $\bar{C}$  with methyl acetoacetate (1:1705) +  $\text{NH}_4\text{OH}$  at  $-1^\circ$  gives (16% yield (137)) 3-carbomethoxy-2,5-dimethylpyrrole [Beil. XXII-29], cryst. from alc., m.p. 119.5°;  $\bar{C}$  with ethyl acetoacetate (1:1710) + excess conc. aq.  $\text{NH}_4\text{OH}$  (138) (140) or in ether with  $\text{NH}_3$  gas (139) gives (yields: 44% (139), 20% (138)) 3-carbomethoxy-2,5-dimethylpyrrole [Beil. XXII-29, XXII-(496)], m.p. 116–117° (138) (other by-prods. also being formed (139));  $\bar{C}$  with ethyl acetoacetate (1:1710) + prim. amines similarly gives *N*-substituted analogs; e.g., use of aq.  $\text{MeNH}_2$  gives (141) 3-carbomethoxy-1,2,5-trimethylpyrrole [Beil. XXII-29, XXII-(496)], m.p. 48° (141); use of aniline gives (139) (141) 3-carbomethoxy-2,5-dimethyl-1-phenylpyrrole [Beil. XXII-30, XXII-(496)], m.p. 43°, b.p. 225° at 40 mm.; for corresp. use of *p*-toluidine see (141).]

[ $\bar{C}$  with ethyl axaloacetate [Beil. III-780, III-(273), III-(479)] in ether treated with  $\text{NH}_3$  gas yields (139) 4-carbomethoxy-5,6-dihydroxy-2-(or 3)-methylpyridine [Beil. XXVII-259], m.p. 223° (139) (much oxamide and other by-prods. also being formed).]

[ $\bar{C}$  with diethyl acetonediacarboxylate (1:1772) in ether (142) (143) (139) or  $\text{C}_6\text{H}_6$  (144) with dry  $\text{NH}_3$  gas gives (yields: 49% (143), 38% (142)) ethyl (3-carbomethoxy-4-methylfuryl-2)acetate [Beil. XVII-333], ad, b.p. 168° at 20 mm. (139).]

[ $\bar{C}$  htd. with amides yields corresp. azazoles: e.g.,  $\bar{C}$  with acetamide htd. 8–10 hrs. at 120° under reflux gives (7% yield (145)) (146) 2,4-dimethylloxazole [Beil. XXVII-17], liq. with odor like pyridine, very vol. aq., b.p. 108° (145) (146);  $\bar{C}$  with benzamide + powdered  $\text{CaCO}_3$  at 115–120° for 8 hrs. gives (15% yield (147)) (148) 2-phenyl-4-methylloxazole [Beil. XXVII-58], b.p. 238–241° (148), 92–95° at 5 mm. (147) ( $\bar{B}.\text{HCl}$ , m.p. 72°,  $\bar{B}.\text{PhOH}$ , m.p. 111° (147)); for corresp. reactn. of  $\bar{C}$  with *m*-nitrobenzamide see (147).]

[ $\bar{C}$  with thioamides yields corresp. thiazoles: e.g.,  $\bar{C}$  with thioformamide in abs. alc. refluxed for 1 hr. (149) or  $\bar{C}$  with formamide +  $\text{P}_2\text{S}_5$  (150) gives (35–47% yield (149)) 4-methylthiazole [Beil. XXVII-16], b.p. 131° (150), 130° (149), 70–71° at 59 mm. (151) ( $\bar{B}.\text{PhOH}$ , m.p. 181° (151);  $\bar{B}.\text{EtI}$ , m.p. 144.5° (149));  $\bar{C}$  with thioacetamide without solvent (152) (153) in aq. or alc. (152) (149) or  $\bar{C}$  with acetamide +  $\text{P}_2\text{S}_5$  (150) yields 2,4-dimethylthiazole [Beil. XXVII-18], b.p. 144–145.5° cor. at 719 mm. (152), 113–141° at 762 mm. (153), 113° (150) (151),  $D_4^0 = 1.0562$  ( $\bar{B}.\text{PhOH}$ , m.p. 137–138° (152),  $\bar{B}.\text{EtI}$ , m.p. 212° dec. (149));  $\bar{C}$  with thioacetamide in alc. gives (155) (147) 4-methyl-2-phenylthiazole [Beil. XXVII-58], m.p. 29.5° (156), b.p. 282° at 762 mm. (156), 275–277° at 750 mm. (147), 111° at 6 mm. (147); many other analogous cases are recorded.)]

[ $\bar{C}$  with aq. thiourea (157) (158) (159) or  $\bar{C}$  with  $\text{NH}_4\text{SCN}$  (160) (161) or  $\bar{C}$  with  $\text{NH}_4\text{SCN}$  +  $\text{NH}_4\text{OH}$  (162) (56) gives (70–75% yield (157)) 2-amino-4-methylthiazole [Beil. XXVII-159], m.p. 44–45° (157), 42° (159), b.p. 231–232° ol. dec. (162), 130–133° at 18 mm. (157), 117–120° at 8 mm. (157);  $\bar{C}$  with *N*-methylthiourea gives (163) (161) (158) 2-(methyl-

amino)-4-methyl-thiazolo [Beil. XXVII-159], pr. from alc., m.p. 71.5-72.5° cor. (163), 64° (164) (B.II Cl, m.p. 228° cor. (163));  $\bar{C}$  with phenylthiourea gives (158) (164) 2-(anilino)-4-methylthiazolo [Beil. XXVII-159], ndls. from alc., m.p. 117-118° (164), 115° (158).]

[ $\bar{C}$  with *O*-methyl thiocarbamate on warming gives (89) 2-methoxy-4-methylthiazolo, b.p. 50-60° at 18 mm. (89) (B.II Cl, m.p. 78°; B.II Cl<sub>2</sub>, m.p. 123-124° (89)) (accompanied by its dimer);  $\bar{C}$  with *O*-ethyl thiocarbamate + KOAc yields (89) 2-ethoxy-4-ethylthiazolo, b.p. 71-72° at 15 mm. (89).]

[ $\bar{C}$  with solid ammonium dithiocarbamate in abs. alc. stood at room temp. for 12 hrs. then refluxed 1 hr. gives (85% yield (151)) 2-mercapto-4-methylthiazolo [Beil. XXVII-161], cryst. from isopropyl ether/alc. or dil. alc., m.p. 80-90° (165), 88.9-88.5° (151); note that in ether these reactants yield (166) an intermediate *S*-acetyl dithiocarbamate, m.p. 80-82° (166), which on stdg. changes to the above 2-mercapto-4-methyl-thiazolo; for use of the latter (or its metal salts) as vulcanization accelerators see (167).]

[ $\bar{C}$  with 1-phenylthiosemicarbazide in abs. alc. readily dis. at room temp. yielding on addn. of pyridino (108) 2-(phenylhydrazino)-4-methylthiazolo, m.p. 170° (acetyl deriv., m.p. 179° (108)); for analogous reactions of  $\bar{C}$  with the three 1-(tolyl)thiosemicarbazides (106), the three 1-(nitrophenyl)thiosemicarbazides (170), see Indic. refs.]

[ $\bar{C}$  with acetone thiosemicarbazone in CHCl<sub>3</sub> gives on warming (171) the corresp. deriv. of 4-methylthiazolone 2, viz., 2-keto-4-methyl-2,3-dihydrothiazolo-2-isopropylidenehydrazone; for analogous reactn. of  $\bar{C}$  with acetophenone thiosemicarbazone and benzaldehyde thiosemicarbazone see (171).]

⑥ Color reactn. with KOH:  $\bar{C}$  with excess very conc. aq. KOH gives crimson red color (5) (22).

— Acetonyl acetate (acetol acetate) (acetoxycetone) [Beil. II-155, II<sub>1</sub>-(72), II<sub>2</sub>-(168)]; b.p. 174-175° at 760 mm. (172), 137-138° at 230 mm. (172),  $D_4^{20} = 1.0749$ ,  $n_D^{20} = 1.4150$  (Beil.). [From  $\bar{C}$  + KOAc in MeOH (173) or abs. EtOH (172) after 2 hrs. reflux (82% yield (173)).]

— Acetonyl benzoate (acetol benzoate) (benzoyloxyacetone) [Beil. IX-148]; m.p. 23.5-24° (174), 25° (175); b.p. 188-190° at 60 mm. (170). [From  $\bar{C}$  with KOBz on htg. together (54% yield (170)) or in alc. soln. (174).]

⑦ 1-( $\beta$ -Naphthoxy)acetone (acetonyl  $\beta$ -naphthyl ether); cryst. from alc., m.p. 78.4° cor. (177), 78° (178), 69-73° (101), 69-72° (70). [From  $\bar{C}$  + Na  $\beta$ -naphtholate on htg. in  $\beta$ -naphthol (178) or from  $\bar{C}$  +  $\beta$ -naphthol (1:1640) + dry K<sub>2</sub>CO<sub>3</sub> refluxed in acetone (21% yield (70)) (note that by addn. of KI yield jumps to 85% (191)).]

⑧ 1-(*N*-phthalimido)acetone (*N*-acetonylphthalimido) [Beil. XXI-477, XXI<sub>1</sub>-(371)]; lfs or ndls. from aq., m.p. 124° (105). [From  $\bar{C}$  + K phthalimido at 120° for 20 min. (176) or refluxed 1 hr. in xylene (97% yield (180)).]

⑨ 1-(*N*-3-antrophthalimido)acetone (*N*-(acetonyl)-3-antrophthalimide; ndls. from alc., m.p. 152-153° (181). [From  $\bar{C}$  with K 3-antrophthalimide on htg. (181).]

⑩ Methylglyoxal dioxime (methylglyoxime) [Beil. I-764, I<sub>1</sub>-(398), I<sub>2</sub>-(822)]; pr. from alc., m.p. 150° (182). [From  $\bar{C}$  with aq. soln. contg. NH<sub>2</sub>OH.HCl (3 moles) + Na<sub>2</sub>CO<sub>3</sub> (2 moles) followed by acidification and ether extraction (182); note that by careful regulation of conditions chloroacetone oxime has been obt'd. (82% yield (183)), but since it is an oil, b.p. 171° at 727 mm. with slight decompn., it has no value as a ⑩ for  $\bar{C}$ .]

⑪ 1-( $\beta$ -Phenylhydrazino)acetone phenylhydrazono [Beil. XV-412]; yel. cryst. from MeOH, m.p. 162.5° (184). [From  $\bar{C}$  with phenylhydrazine (3 moles) in abs. alc. at -10 to -18° (184).]

⑫ Chloroacetone *o*-nitrophenylhydrazone: m.p. 83° (135).

- ③ Chloroacetone 2,4-dinitrophenylhydrazone: yel. ndls. from alc., m.p. 124.0–125.5° (185) (51), 124° (39). [From  $\bar{C}$  (0.5 g.) with 2,4-dinitrophenylhydrazine (1.0 g.) in alc. (12 ml.) + conc. HCl (1.5 g.) under reflux (185); note that this prod. on protracted (13 hrs.) boilg. in alc. disproportionates yielding (185)  $\bar{C}$  + 2,4-dinitrophenylhydrazine (both sol. hot alc.) accompanied by the spar. sol. methylglyoxal-bis-(2,4-dinitrophenyl)-osazone, cryst. from pyridine, m.p. 298° (185), for various other reactans. see (185).]
- ④ Chloroacetone semicarbazone: m.p. 147–148° dec. (39), 141–142° (47), 136–137° (48), 165° (50), 163–165° (44). [From  $\bar{C}$  with aq. semicarbazide HCl on addn. of solid  $\text{NaHCO}_3$  at room temp. (186); note that this prod. is reactive and on boilg. with aq. dissolves to a bright yel. soln. which soon becomes colorless and on ppts. hydrazine dicarboxylic acid diamide leaving in the filtrate hydroxypropanone semicarbazone, m.p. abt. 192° dec. (186); these changes (which doubtless occur slowly even on standing in water at room temp.) probably account for the divergent values of m.p. reported above.]
- ⑤ Condensation prod. ( $\text{C}_{17}\text{H}_{20}\text{O}_4\text{N}_2\text{S}$ ) of  $\bar{C}$  with *N*-methyl- $\beta$ -carbobyhydrazidopyridinium *p*-toluenesulfonate: cryst. from 1:1 alc./ether, m.p. 135° cor. (187). [From  $\bar{C}$  + indicated react. in abs. alc. on refluxing 15 min. (187).]

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(other prods. are also formed) or by electrolysis in HCl (9) see indic. refs.; from ethyl  $\alpha,\alpha$ -dichloroacetate [Beil. III-663, III<sub>1</sub>-(233), III<sub>2</sub>-(427)] by ketonic cleavage with dil. HCl in s.t. at 170–180° for 4–6 hrs. (14) or by refluxing 4–5 hrs. with HCl (15) cf. (4) see indic. refs.; for formn. of  $\bar{C}$  from isopropyl alc. (1:6135) with Cl<sub>2</sub> see (16); from methylacetylene with HOCl (42% yield) see (17); from 1,1-dichloro-2-methylpropene-2 (3:7480) with O<sub>3</sub> see (18); from homocaspic acid [Beil. IV-494, IV<sub>1</sub>-(541), IV<sub>2</sub>-(912)] by oxidn. with sodium *N*-chloro-*p*-toluenesulfonamide see (19).]

[ $\bar{C}$  on reduction with Al(OEt)<sub>3</sub> + anhydrous acetaldehyde in dry ether gives (45% yield (20)) 1,1-dichloropropanol-2 (3:5755), h.p. 146–148°. —  $\bar{C}$  on reduction by yeast gives (54% yield (21)) levorotatory 1,1-dichloropropanol-2.]

$\bar{C}$  on oxidn. with conc. HNO<sub>3</sub>, CrO<sub>3</sub>, or KMnO<sub>4</sub> yields (22) dichloroacetic acid (3:6208).

[ $\bar{C}$  with Br<sub>2</sub> (1 mole) (1) yields 3-bromo-1,1-dichloropropanone-2 [Beil. 1-657], b.p. 111° at 25 mm. (1);  $\bar{C}$  with excess Br<sub>2</sub> at 100° yields (1) 3,3-dibromo-1,1-dichloropropanone-2 [Beil. 1-658], b.p. 120° at 25 mm. (1); for study of rate of bromination of  $\bar{C}$  and influence of catalysts thereon see (4).]

[ $\bar{C}$  with PCl<sub>5</sub> htd. at b.p. of mixt. for 2 days yields (2) 1,1,2,2-tetrachloropropane (3:5825), b.p. 153°.]

[ $\bar{C}$  with aq. in s.t. at 200° for 6 hrs. yields (23) lactic acid (1:0400). —  $\bar{C}$  with aq. alk. yields (presumably via cleavage of the expected methylglyoxal) acetic acid (1:1010) and formic acid (1:1005); by virtue of this result  $\bar{C}$  readily reduces Fehling's soln. (24). —  $\bar{C}$  with aq. 10% K<sub>2</sub>CO<sub>3</sub> on boilg. loses HCl yielding (25) acrylic acid (1:1020).]

$\bar{C}$  with satd. aq. NaHSO<sub>3</sub> soln. readily yields (1) (5) an addo. prod. crystg. as a trihydrate.

[ $\bar{C}$  with conc. aq. HCN slowly dis. on protracted refluxing yielding (10) the corresp. cyanohydrin ( $\beta,\beta$ -dichloro- $\alpha$ -hydroxy-isobutyronitrile) [Beil. III-318], an oil, which on htg. dissociates into its components; this prod., however, on hydrolysis with strong HCl yields (10) the corresp. acid,  $\beta,\beta$ -dichloro- $\alpha$ -hydroxyisobutyric acid (3:2145), pr. from alc./ether or cryst. from C<sub>6</sub>H<sub>6</sub>, m.p. 82–83° (10) (20). — Note also that  $\bar{C}$  with *p*-benzylisocyanide + aq. on stdg. yields (20)  $\beta,\beta$ -dichloro- $\alpha$ -hydroxy-isobutyranilide, pr. from CHCl<sub>3</sub>, m.p. 132–133° (26).]

[ $\bar{C}$  in excess MeOH (5 moles) with ethyl iminoformate hydrochloride (1 $\frac{1}{4}$  moles) 4–8 days at room temp. yields (27) *unsym.*-dichloroacetone dimethylacetal, b.p. 170–171° at 767 mm., 63° at 0 mm. —  $\bar{C}$  in excess EtOH with ethyl iminoformate as above yields (27) *unsym.*-dichloroacetone diethylacetal, b.p. 183–184° at 767 mm., 76° at 8 mm.)]

[ $\bar{C}$  with *o*-nitrobenzaldehyde in alc. treated dropwise with aq. 5% NaOH condenses yielding (28)  $\omega,\omega$ -dichloro-*o*-nitrobenzalacetone, pptd. as oil by addn. of aq., colorless pr. from C<sub>6</sub>H<sub>6</sub>, m.p. 106–107° (28). — By similar procedure  $\bar{C}$  with *m*-nitrobenzaldehyde gives (28)  $\omega,\omega$ -dichloro-*m*-nitrobenzalacetone, colorless pr. from C<sub>6</sub>H<sub>6</sub>, m.p. 116–117°;  $\bar{C}$  with *p*-nitrobenzaldehyde similarly gives (30% yield (28))  $\omega,\omega$ -dichloro-*p*-nitrobenzalacetone, colorless pr. from C<sub>6</sub>H<sub>6</sub> or ether, m.p. 125°.]

[ $\bar{C}$  with diazotized aniline in pres. of NaOAc yields (29) dichloro-*bis*-(benzeneazo)-methane, yel.-or. cryst. from hot alc., m.p. 81–82°;  $\bar{C}$  with diazotized *p*-toluidine in pres. of NaOAc yields (29) dichloro-*bis*-(*p*-tolueneazo)methane, or. cryst. from C<sub>6</sub>H<sub>6</sub>, m.p. 159–160°.]

$\bar{C}$  (1 mole) treated with aq. soln. of excess NH<sub>2</sub>OH.HCl (6 moles) + Na<sub>2</sub>CO<sub>3</sub> (3 moles), stood 24 hrs., and acidified yields (15) methylglyoxal dioxime (methylglyoxime) [Beil. 1-764, I<sub>1</sub>-(396), I<sub>2</sub>-(822)], pr. from alc. or aq., m.p. 157°, 153° (15) (30); the same prod. also results if a satd. soln. hydroxylamine sulfate is used (30) in place of free hydroxylamine.

$\bar{C}$  (1 g.) in abs. alc. (20 g.) with *p*-benzylhydrazine (2.5 g.) stood for 1 $\frac{1}{2}$  days, then warmed with aq. (100 ml.), yields (31) as insol. residue (1 g.) methylglyoxal *bis*-(*p*-benzyl)osazone [Beil. XV-156, XV<sub>1</sub>-(38)], yel. ndls. from dil. alc., m.p. 148° (31).]

⑤ 1,1-Dichloropropanone-2 semicarbazone: m.p.  $163^\circ$  (32). [From  $\bar{C}$  in alc. with aq. semicarbazide.HCl (1 mole) without addn. of NaOAc, the semicarbazone pptg. immediately; note, however, that on stdg. the filtrate ppts. a small amt. of methylglyoxal bis-semicarbazone, m.p.  $251^\circ$ , also formed (together with equiv.  $\bar{C}$ ) on boilg. the semicarbazone with aq. (32).]

3:5430 (1) Cloëz, *Ann. chim.* (6) 9, 164-165, 175-176, 211-213 (1886). (2) Borsche, *Fittig, Ann.* 133, 112-117, 124 (1865). (3) Cheng, *Z. physik. Chem.* B-26, 296 (1934). (4) Bell, *Ladwell, Proc. Roy. Soc. London*, A-176, 104-106 (1940). (5) Fittig, *Ann.* 110, 38-43 (1859). (6) Harkins, Clark, Roberts, *J. Am. Chem. Soc.* 42, 703 (1920). (7) Glutz, Fischer, *J. prakt. Chem.* (2) 4, 53 (1871). (8) Mulder, *Ber.* 5, 1007-1009 (1872). (9) Theegarten, *Ber.* 6, 897-898 (1873). (10) Bischoff, *Ber.* 8, 1330-1336 (1875).

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(28) Heller, *Ann.* 375, 287-288 (1910). (29) Knöpper, *Monatsh.* 32, 765-766 (1911).

3:5450 1,3-DICHLOROPROPANE  $ClCH_2CH_2CH_2Cl$   $C_3H_6Cl_2$  Bell, I- 105  
(Trimethylene (di)chloride) I-( 34)  
I-( 73)

B.P.	F.P.
120.5-120.6° (1) (2) (3) (4)	$-99.5^\circ$ (8) $D_4^{25} = 1.1770$ (11) $n_D^{25} = 1.4362$ (12)
120.4° at 760 mm. (5)	
(6) (7)	$D_4^{17.6} = 1.1896$ (13) $n_D^{20} = 1.452$ (9)
120.3-120.5° at 760 mm. (8)	1.44867 (28)
120.2° at 750 mm. (28)	
119.2° at 740 mm. (9)	
119° at 740 mm. (10)	

Colorless oil. — Note that b.p. of  $125^\circ$  given in I.C.T. is too high (4). — Almost insol. in aq. [for precise data see (1) (2) (3) (4)].

[For prepn. from propanediol-1,3 (trimethylene glycol) (1:6490) with fung. HCl in s.t. at  $100^\circ$  (13) (10) (20-25% yield (14)) but always accompanied by 3-chloropropanol-1 (trimethylene chlorohydrin) (3:8285) see indic. refs.; with  $PCl_3 + ZnCl_2$  (21% yield (15)), or  $PCl_3 + ZnCl_2$  (31% yield (15)), or  $SOCl_2$  (50% yield (15)) see (15); for prepn. of  $\bar{C}$  from 1,3-dibromopropane (trimethylene dibromide) +  $HgCl_2$  (8) (10) or 1,3-diiodopropane +  $AgCl$  (16) see indic. refs.; for prepn. of  $\bar{C}$  from  $\gamma$ -chloropropyl *p*-toluenesulfonate with various  $RMgX$  cpds see (12); for formn. of  $\bar{C}$  (193% (7) together with other products) by chlorination of propane (17) (18) (19) or *n*-propyl chloride (3:7040) (17) (18) see indic. refs.]

[ $\bar{C}$  with Zn dust in aq. alc. (20) (21) or better in a high-boilg. solvent (7) (22) yields cyclopropane, b.p.  $-34^\circ$ .]

$\bar{C}$  with alc. KOH yields allyl chloride (3:7035), b.p.  $46^\circ$ , which then reacts with the KOEt yielding (10) allyl ethyl ether (1:7850), b.p.  $66-67^\circ$  at 742 mm.

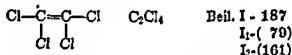
⑥ 1,3-Diphenoxypropane (1:7170) q.v.: lfts. from alc., m.p.  $61^\circ$  (23),  $60-61^\circ$  (24),  $59-60^\circ$  (25); b.p.  $338-340^\circ$  cor. at 762 mm. (26). [From  $\bar{C}$  (26) (or trimethylene dibromide (24) or trimethylene diiodide (25)) with sodium phenolate.]

⑦ 1,3-Di-( $\alpha$ -naphthoxy)propane [Beil. VI-607]: ndls. from alc., m.p.  $103-104^\circ$  (27).

⑧ 1,3-Di-( $\beta$ -naphthoxy)propane [Beil. VI-642]: lfts. from AcOH, m.p.  $148-149^\circ$  (27).

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3:5400 TETRACHLOROETHYLENE  
(Perchloroethylene)



B.P.	F.P.			
121.20°	at 760 mm. (1)	-23.5° (16)	$D_4^{25} = 1.01403$ (1)	$n_D^{25} = 1.4603$ (22)
121.1°	at 760 mm. (2)	-23° (17)		
	(3) (4)			
121°	at 765 mm. (5)	-22.35° (1)	$D_4^{20} = 1.0230$ (13)	$n_D^{20} = 1.5058$ (13)
121°	at 760 mm. (6)	(8)	1.023 (6)	1.50566 (2)
121°	(7)	-22.4° (18)	1.02286 (1)	1.50547 (20)
120.8°	at 760 mm. (8)	-19° (10)	1.0226 (20)	
120.74°	(9)		1.0207 (2)	
120.5-120.8° at 770 mm. (10)				
116.5-120.5° at 747 mm. (20)			$D_4^{15} = 1.03166$ (1)	$n_D^{15} = 1.50812$ (1)
116.0-120.6° u.c. (11)			1.0236 (14)	1.50831 (1)
116-120° at 753 mm. (12)				1.50896 (1)
118-120.5° (13)				
118.5° at 751 mm. (14)			$D_4^{12.5} = 1.0232$ (21)	
118.0-118.1° at 740 mm. (15)				$n_D^{12.5} = 1.5087$ (21)
33.2° at 30 mm. (14)				
See also Note 1.				
See also Note 2.				

Note 1. For vap. press. of  $\bar{C}$  from 33-118° see (14). Note 2. For  $D_4^t$  over range  $t = 15-90^\circ$  see (14).

Colorless liq. widely used as solvent, etc. (see also below). —  $\bar{C}$  is pract. insol. aq., but detailed studies do not appear to be recorded. —  $\bar{C}$  is miscible with alc., ether,  $\text{CHCl}_3$ ,  $\text{C}_6\text{H}_6$ , and many other org. solvents.

### GENERAL

[For study of  $\bar{C}$  as solvent for detn. of mol. wts. by raising of b.p. (ebullioscopic const. =  $55.0^\circ$  per mole solute/100 g.  $\bar{C}$ ) see (23). — For study of thermal conductivity see (24). — For soly. in  $\bar{C}$  of gaseous  $\text{HCl}$ ,  $\text{H}_2\text{S}$ , or  $\text{NH}_3$  see (11). — For study of influence of  $\bar{C}$  upon inflammability of mixts. of air with  $\text{CH}_4$  (25) (10) (26) (27), with  $\text{CO}$  (10) (28), with  $\text{H}_2$  (10), or acetylene (10) see indic. refs.]

Binary systems contg.  $\bar{C}$ . [System  $\bar{C} + \text{CCl}_4$  for f.p./compn. data see (18); for  $n_D^{25}$ /compn. and use in anal. of the system see (22); for vap. press. and liq./vapor compn. of system see (29). — System  $\bar{C} + 1,1,2,2\text{-tetrachloroethane}$  (3:5750): for f.p./compn. data see (17). — System  $\bar{C} + \text{pentachloroethane}$  (3:5880): for f.p./compn. data (eutectic, f.p.  $-54.8^\circ$  contg. 58.4 wt. %  $\bar{C}$ ) see (18). — System  $\bar{C} + \text{isopropyl alc.}$  (1:6135); for  $D_{25}^{25}$ /compn. and  $n_D^{25}$ /compn. data see (30)]

$\bar{C}$  forms binary azeotropes with many alcohols [e.g.,  $\bar{C}$  with  $\text{MeOH}$  (1:6120) forms a const.-boilg. mixt., b.p.  $63.75^\circ$  at 760 mm., contg. 36.5 wt. %  $\bar{C}$  (3);  $\bar{C}$  with  $\text{EtOH}$  (1:6130) forms a const.-boilg. mixt., b.p.  $70.75^\circ$  at 760 mm., contg. 37 wt. %  $\bar{C}$  (3);  $\bar{C}$  with  $n\text{-propyl alc.}$  (1:6150) forms a const.-boilg. mixt., b.p.  $94.05^\circ$  at 760 mm., contg. 52 wt. %  $\bar{C}$  (31);  $\bar{C}$  with  $\text{isopropyl alc.}$  (1:6135) forms a const.-boilg. mixt., b.p.  $81.7^\circ$  at 760 mm., contg. 30 wt. %  $\bar{C}$  (31),  $\bar{C}$  with  $n\text{-butyl alc.}$  (1:6180) forms a const.-boilg. mixt., b.p.  $108.95^\circ$  at 760 mm., contg. 71 wt. %  $\bar{C}$  (3);  $\bar{C}$  with  $\text{isocamyl alc.}$  (1:6200) forms a const.-boilg. mixt., b.p.  $110.1^\circ$  at 760 mm., contg. 80 wt. %  $\bar{C}$  (31);  $\bar{C}$  with  $\text{ethylene glycol}$  (1:6465) forms a const.-boilg. mixt., b.p.  $119.1^\circ$  at 760 mm., contg. 94 wt. %  $\bar{C}$ ].

$\bar{C}$  forms binary azeotropes with many other org. cpds. [e.g.,  $\bar{C}$  with  $\text{formic acid}$  (1:1005) forms a const.-boilg. mixt., b.p.  $88.15^\circ$  at 760 mm., contg. 50 wt. %  $\bar{C}$  (32);  $\bar{C}$  with  $\text{AcOH}$  (1:1010) forms a const.-boilg. mixt., b.p.  $107.35^\circ$  at 760 mm., contg. 61.5 wt. %  $\bar{C}$  (218);  $\bar{C}$  with  $\text{propionic acid}$  (1:1025) forms a const.-boilg. mixt., b.p.  $119.15^\circ$  at 760 mm., contg. 91.5 wt. %  $\bar{C}$  (4);  $\bar{C}$  with  $\text{isobutyric acid}$  (1:1030) forms a const.-boilg. mixt., b.p.  $120.5^\circ$ , contg. 97 wt. %  $\bar{C}$  (33)]

Uses of  $\bar{C}$ .  $\bar{C}$  because of its solvent properties, b.p., unflammability, and immiscibility with aq., etc., finds wide use. — [Other examples of its utility include the following: for use as dry-cleaning solvent see (34), cf. (35) (36) (222); for use with lower aliph. alcs. as solv. for cellulose ethers see (37); for use in dewaxing of lubricating oil see (38); for use in liq.  $\text{HCN}$  to diminish inflammability and explosiveness see (39); for use as a component of comml. tear-gas mixts. see (40).]

[For study of use of  $\bar{C}$  as an anesthetic (41), as fumigation agt. (with  $\text{CCl}_4$ ) for grain or flour (42), for sterilization of surgical catgut (43), of antiseptic action (compared with  $\text{CHCl}_3$  (44)) (45) see indic. refs.]

[For examples of studies of use of  $\bar{C}$  as anthelmintic especially with reference to book-worm and similar parasites see (46)–(57) incl.; for comparison of anthelmintic action of  $\bar{C}$  with that of  $\text{CCl}_4$  (58) (59) or of chenopodium oil (60) see indic. refs.; for patent prepn. of  $\bar{C}$  for use as anthelmintic see (61).] (For toxicity see below.)

[For use of  $\bar{C}$  as the "booster" liquid in detn. of aq. by distn. especially in molasses and other sugar industry products see (62) (63) (64) (65) (66) (67). — For use of  $\bar{C}$  in prepn. of anhydrous  $\text{Na}_2\text{O}_2$  by removal of moisture by distn. see (68).]

[For brief general surveys of  $\bar{C}$  see (69) (70).]

Physiological actn. and/or toxicity of  $\bar{C}$ . [For studies from various viewpoints on toxicity of  $\bar{C}$  see (57), (71)–(82) incl., also especially (219) (220) (224).]

Determination of  $\bar{C}$ .  $\bar{C}$  is usually detd. by some form of decn. followed by volumetric or gravimetric detn. of resultant chloride ion [e.g., for methods involving decn. of  $\bar{C}$  with  $\text{Na} + \text{AmOH}$  in xylene (83) (84), with  $\text{Na} + \text{ethanolamine}$  in dioxane soln. (55) (223), or with  $\text{Na}$  in liq.  $\text{NH}_3$  (86) (note that some cyanide formn. occurs) see indic. refs.; for methods involving thermal decn. see (57) (215)].

[For detn. of  $\bar{C}$  by means of a recording ultra-violet photometer (the R. + H. Tri-Per Analyzer) see (88).]

### PREPARATION OF $\bar{C}$

From various polychloroethanes or polychloroethylenes. [For prepn. of  $\bar{C}$  from hexachloroethane (3:4835) by pyrolysis at  $565^\circ$  (89-94% conversion (59)), by passing over porcelain chips in hot tube (90) (note that  $\text{CCl}_4$  (3:5100) is also formed), or by passing with  $\text{H}_2$  over  $\text{Ni}$  at  $270^\circ$  (91) see indic. refs.; for prepn. of  $\bar{C}$  from hexachloroethane (3:4835) by treatment with granulated  $\text{Zn}$  in boilg. alc. (7), with  $\text{Zn} + \text{dil. H}_2\text{SO}_4$  at room temp. for several days (100% yield (5)) (92) (116), or even with  $\text{Zn} + \text{aq. above } 80^\circ$  (33), with alc.  $\text{KSH}$  (94), with molecular  $\text{Ag}$  at  $280^\circ$  in s.t. (95), with  $\text{SbF}_3$  at  $300-325^\circ$  under press. (96), with acetylene over activated carbon at  $200-400^\circ$  (97) cf. (123), with aniline at  $170^\circ$  at ord. press. (7), with  $\text{N}/10$  abs.  $\text{EtOH}/\text{NaOH}$  at  $25^\circ$  (216), or with alc. free  $\text{NaOEt}$  in ether under press. at  $140^\circ$  (217) see indic. refs.]

[For prepn. of  $\bar{C}$  from pentachloroethane (3:5880) by elimination of 1  $\text{HCl}$  in various ways: e.g., by passing over bone char at  $280^\circ$  (98), or over  $\text{NiCl}_2$  at  $330^\circ$  (99), by htg. with  $\text{AlCl}_3$  at  $70-100^\circ$  (100% yield (101)) (100) or under reflux (102), with liq.  $\text{NH}_3$  at  $-18$  to  $-34^\circ$  under reduced press. (103) (104), with  $\text{MeOH}$  over  $\text{Al}_2\text{O}_3$  at  $290^\circ$  ( $\text{MeCl}$  (3:7005) is also formed) (105), with acetylene over cat. at  $200-300^\circ$  (vinyl chloride (3:7010) is also formed) (106), with alc.  $\text{KOH}$  (107) (108), or in alc. with 2  $\text{N}$  aq.  $\text{NaOH}$  in cold (98% yield) (109) see indic. refs.]

[For prepn. of  $\bar{C}$  from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) (see also below under prepn. of  $\bar{C}$  from acetylene) on pyrolysis at  $700^\circ$  (110), with air over pumice +  $\text{CuCl}_2$  at  $430-450^\circ$  (111), or with  $\text{Cl}_2$  over activated carbon contg. 30%  $\text{CuCl}_2$  at  $300-320^\circ$  (112) see indic. refs.]

[For prepn. of  $\bar{C}$  from 1,2-dichloroethane (ethylene dichloride) (3:5130) with  $\text{Cl}_2$  over cat. at  $300-500^\circ$  see (113); from ethane or its chloro deriva. with  $\text{Cl}_2 + \text{fused metal chlorides}$  such as  $\text{AlCl}_3$ , etc., at  $250-500^\circ$  see (114).]

[For formn. of  $\bar{C}$  from trichloroethylene (3:5170) on pyrolysis at  $700^\circ$  (110) or with anhyd.  $\text{FeCl}_3$  on htg. see (115).]

From various polychloromethanes. [For prepn. of  $\bar{C}$  from  $\text{CCl}_4$  (3:5100) through tube at  $1300-1400^\circ$  see (116) (117); for formn. of  $\bar{C}$  (together with other prods.) from  $\text{CCl}_4 + \text{H}_2$  through hot tube over pumice at low red heat (118) or through tube at  $600-650^\circ$  (119), or in dark electric discharge (120), see indic. refs. — Note also that  $\bar{C}$  has been found (121) as a by-prod. of prepn. of  $\text{CCl}_4$  (3:5100) by actn. of  $\text{Cl}_2$  on  $\text{CS}_2$ .]

[For formn. of  $\bar{C}$  from  $\text{CHCl}_3$  (3:5050) +  $\text{H}_2$  in dark electric discharge see (120).]

From acetylene with  $\text{Cl}_2$  (see also above under prepn. of  $\bar{C}$  from 1,1,2,2-tetrachloroethane (acetylene tetrachloride)). [For prepn. of  $\bar{C}$  from acetylene with  $\text{Cl}_2 + \text{inert gas}$  over cat. at  $250-400^\circ$  see (122) (123) (124) (125); from acetylene with  $\text{Cl}_2$  at  $700-900^\circ$  in absence of extraneous substances (126); from acetylene with  $\text{Cl}_2$  see (127) (128); from acetylene with  $\text{Cl}_2$  in halogenated solv. at  $175-260^\circ + \text{AlCl}_3$ , etc., see (129).]

From miscellaneous sources. [For prepn. of  $\bar{C}$  from  $\text{CO} + \text{HCl}$  over cat. at  $230-240^\circ$  under high press. ( $\text{CHCl}_3$  is also formed) see (130); from *unsym.*-heptachloropropene (3:0200) by dissociation into  $\bar{C} + \text{CHCl}_3$  over  $\text{Cu}_2\text{Cl}_2$  at  $250^\circ$  see (131); from chloral (3:5210) by long boilg. with  $\text{AlCl}_3$  see (132) cf. (133) (134); from tetrachloroethyl chloro-

formate with  $\text{AlCl}_3$  see (135); from trichloroacetic acid (3:1150) over  $\text{ThO}_2 + \text{kaolin}$  at 230–250° see (136); from pentachloropropionic acid (3:4895) on htg. in aq. (137), or from its ferric salt in light (139) cf. (140), or from pentachloropropionyl chloride (3:0470) with  $\text{AlCl}_3$  (1 mole) at 60° (138) see indic. refs.]

### PURIFICATION OF $\bar{\text{C}}$

Comml.  $\bar{\text{C}}$  conts. some impurity which readily chlorinates (15); note also that  $\bar{\text{C}}$ , especially if exposed to light and air, may contain phosgene (3:5000), trichloroacetyl chloride (3:5420), trichloroacetic acid (3:1150), and other prods.; cf. below under oxidation of  $\bar{\text{C}}$ . — [For purification of  $\bar{\text{C}}$  by treatment with  $\text{Cl}_2$  followed by illumination (15), by treatment with aq. alk. at elev. temp. (for removal of 1,1,2-trichloroethane (3:5330) or 1,1,1,2-tetrachloroethane (3:5555)) (141), by refluxing with finely divided metals + dil. acid (142) or with 1% Al or  $\text{AlCl}_3$  (143), or by passing vapor over kaolin at 250° (144), see indic. refs.]

### STABILIZATION OF $\bar{\text{C}}$

To increase the resistance of  $\bar{\text{C}}$  to photooxidation (see below) and other changes, the addition of very small amts. of various stabilizers has been recommended. — [For example, for study of control of photooxidation of  $\bar{\text{C}}$  by use of inhibitors such as thymol (1:1430), ether, alcohol, thiourea, etc., see (145). — For stabilization of  $\bar{\text{C}}$  by addn. of small amts. of paraffin hydrocarbons (e.g., gasoline) (146), various phenols (such as hydroquinone monomethyl or monobenzyl ether) (147), oil-sol. azo dyes contg. phenolic groups (148), mercaptans (such as *n*-butyl mercaptan) (149), various org. tertiary amines such as triethylamine (150) or picoline (151), various phenols, amines, and aminophenols (152), or a wide variety of org. *N* cpds. (221) see indic. refs.]

### CHEMICAL BEHAVIOR OF $\bar{\text{C}}$

**Pyrolysis.** [ $\bar{\text{C}}$  on pyrolysis over heated Pt wire gives (153) (154) hexachloroethane (3:4835) + hexachlorobenzene (3:4939) +  $\text{Cl}_2$ .]

**Hydrogenation.** [Note that  $\bar{\text{C}}$  does not add  $\text{H}_2$  even in pres. of Ni at 300–350° (99);  $\bar{\text{C}}$  with excess  $\text{H}_2$  over Ni at 220° dec. (163) to carbon +  $\text{HCl}$ .]

**Oxidation.**  $\bar{\text{C}}$  can be oxidized especially in the presence of light and moisture giving according to conditions trichloroacetyl chloride (3:5420), phosgene (3:5000), trichloroacetic acid (3:1150), or various mixtures of these prods.; for inhibition of this oxidation see above under stabilization of  $\bar{\text{C}}$

[For extensive studies of photochem. oxidn. of  $\bar{\text{C}}$  giving 87% trichloroacetyl chloride accompanied by phosgene see (15) (155) (156); for oxidn. of  $\bar{\text{C}}$  on stdg. with aq. in light for 4 months yielding trichloroacetic acid see (157) cf. (158); for oxidn. of  $\bar{\text{C}}$  to trichloroacetyl chloride with  $\text{O}_3$  (159) (160), with peracetic acid (acetyl hydrogen peroxide) (161), with conc.  $\text{HNO}_3 + \text{conc. H}_2\text{SO}_4$  in freezing mixt. (162), with  $\text{SO}_3$  at 150° (164), or with  $\text{N}_2\text{O}_5$  (194) see indic. refs.; for patents on photochem. oxidn. of  $\bar{\text{C}}$  to trichloroacetyl chloride (3:5420) see (165) (166).]

[ $\bar{\text{C}}$  on oxidn. with  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$  is completely converted to  $\text{CO}_2 + \text{H}_2\text{O} + \text{HCl}$  (167);  $\bar{\text{C}}$  passed with air over  $\text{CuO}$  at 450° gives only traces (168) of phosgene.]

**Reaction with halogens.** [ $\bar{\text{C}}$  dislvd. in dichlorodifluoromethane ("Freon") with  $\text{F}_2$  at –80° (169), or  $\bar{\text{C}}$  with  $\text{F}_2$  at 0° directly (170) but not in  $\text{CCl}_4$  soln. (169) cf. (172), or  $\bar{\text{C}}$  in vapor phase at 130° with  $\text{F}_2$  diluted with  $\text{N}_2$  (171), gives (20% yield (171)) 1,2-difluoro-1,1,2,2-tetrachloroethane, m.p. 26.5° (96) (169), accompanied by various other prods. such as fluoropentachloroethane, m.p. 99.0–99.5° (in s.t.), b.p. 136–138° (170), and 1,4-difluoro-octachlorobutane (170) (169), m.p. 4–5° (170), h.p. 152.2° at 20 mm.,  $D_4^{20} = 1.9272$ ,  $n_D^{20} = 1.5256$  (170).]

[ $\bar{C}$  with dry  $Cl_2$  in direct sunlight (90), or  $\bar{C}$  in  $CCl_4$  at  $22^\circ$  (173) or in vapor phase at  $40^\circ$  and low press. (155) in light and absence of  $O_2$ , or  $\bar{C}$  with  $SO_2Cl_2$  in pres. of dibenzoyl peroxide (174) adds  $Cl_2$  yielding hexachloroethane (3:4835) q.v.; note, however, that  $\bar{C} + Cl_2 +$  light in pres. of  $O_2$  undergoes photooxidation to trichloroacetyl chloride (see above under oxidation of  $\bar{C}$ ). —  $\bar{C}$  with  $Cl_2$  at  $700-800^\circ$  (175), or  $\bar{C}$  with  $Cl_2$  over act. carbon at  $600-650^\circ$  (176), undergoes cleavage of  $C-C$  bond yielding  $CCl_4$  (3:5100); for study of this reactn. see (177).]

[ $\bar{C}$  with  $Br_2$  in sunlight adds 1 mole  $Br_2$  yielding (178) (179) (110) 1,2-dibromo-1,1,2,2-tetrachloroethane, m.p.  $197.5^\circ$  dec. (in s. cap. tube) (180),  $200-205^\circ$  dec. (110),  $190^\circ$  dec. (138). — Note, however, that this photochem. addn. is inhibited by its reactn. prod. (181), that, although accelerated by small amts.  $O_2$ , pres. of large amts.  $O_2$  lead to a halogen catalyzed photooxidation (181), that in  $CCl_4$  soln. resultant equilibrium mixt. conts. only 30% addn. prod. (182). — For extensive study of this reactn. see (181); for studies of its rate see (183) (184); for extensive study of photochem. dissoc. of prod. see (179). — For study of reactn. of  $\bar{C}$  with radio-bromine see (185).]

[ $\bar{C}$  does not add  $I_2$ . — For soly. of  $I_2$  in  $\bar{C}$  see (186); for use of such solns. in detn. of iodine number of unsatd. oils and fats see (187) (188).]

Behavior of  $\bar{C}$  with other inorganic materials. [ $\bar{C}$  with  $Cl_2O$  in  $CCl_4$  at  $-20^\circ$  gives (189) hexachloroethane (3:4835).]

[ $\bar{C}$  with  $NO_2$  in s.t. at  $100-120^\circ$  for 3 hrs. (190), or at  $100-110^\circ$  for 3 hrs. (5), or at  $80^\circ$  for 3 hrs. or  $60^\circ$  for 6 hrs. (191), or at 10–12 atm. press. at  $60-80^\circ$  for 3–6 hrs. (191), or  $\bar{C}$  with fuming  $HNO_3$  at ord. temp. stood several days (5) cf. (192), adds 2 moles  $NO_2$  yielding 1,2-dinitro-1,1,2,2-tetrachloroethane [Beil. I-102, I<sub>1</sub>-(33)], cryst. from alc., m.p.  $142-143^\circ$  (s. cap. tube) (5).]

[ $\bar{C}$  with nitryl chloride ( $ClNO_2$ ) yields (193) 1-nitro-1,1,2,2,2-pentachloroethane, lts. from alc., m.p.  $192^\circ$  (s. cap. tube) (193).]

[ $\bar{C}$  with  $N_2O_5$  undergoes vigorous oxidn. (presumably to trichloroacetyl chloride) (194).]

[ $\bar{C}$  with  $NH_3$  at  $700-800^\circ$  splits off all its halogen as  $NH_4Cl$  (195) cf. (196).]

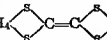
[For behavior of  $\bar{C}$  with various common metals see (197); note that  $\bar{C}$  is not attacked by molecular Ag even at  $300^\circ$  (95); note that  $\bar{C}$  with Na or K or their mixture may (like many other polychloro compds.) explode under certain conditions (for an extensive study see (198)).]

Behavior of  $\bar{C}$  with organic reactants. [ $\bar{C}$  (1 mole) with  $CHCl_3$  (3 moles) +  $AlCl_3$  (0.2 mole) refluxed 15–20 hrs. gives (85–93% yield (199)) (101) (16) (200) (201) (202) (214) *unsym.*-heptachloropropane (3:0200); for study of equilibrium of system  $\bar{C} + CHCl_3 +$  *unsym.*-heptachloropropane see (131).]

[ $\bar{C}$  with 1,1,2,3,3-pentachloropropene-1 (3:6075) +  $AlCl_3$  gives (201) cf. (214) 1,1,3,4,5,5,6,6,6-nonachloropentene-1.]

[ $\bar{C}$  with  $NaOEt$  at  $100-120^\circ$  yields (203) ethyl dichloroacetate (3:5850) + Na diethoxyacetate + other prods., presumably via ethyl  $\alpha,\beta,\beta$ -trichlorovinyl ether,  $\alpha,\alpha$ -dichloro- $\beta,\beta$ -diethoxyethylene, triethyl dichloroorthoacetate, etc., cf. (204).]

[ $\bar{C}$  (1 mole) with  $NaSC_6H_5$  (2 moles) in alc., refluxed 48 hrs., gives (yield not stated (205))  $\alpha,\beta$ -dichloro- $\alpha,\beta$ -bis-(thiophenyl)ethylene, ndls. from alc., m.p.  $71-72^\circ$  (205). —  $\bar{C}$  with disodium salt of dithiopyrocatechol in alc. at  $110-120^\circ$  in s.t. for 7 hrs. gives small

yield (206) of  $C_6H_4$    $C_6H_4$ , golden ndls., m.p.  $234^\circ$  (206).]

[ $\bar{C}$  with paraformaldehyde (1:0080) + conc.  $H_2SO_4$  as directed (207) gives  $\alpha,\alpha$ -dichloro- $\beta$ -hydroxypropionic acid, m.p.  $88-89^\circ$  (s. cap. tube).]

[ $\bar{C}$  with dibenzoyl peroxide on refluxing either with or without  $AlCl_3$  gives (40% yield

(20S))  $\alpha, \alpha, \beta$ -trichloro- $\beta$ -pbcnylethylene ( $\alpha, \alpha, \beta$ -trichlorostyrene) [Beil. V-477,  $V_2$ -(367)], b.p. 87–89° at 3 mm.,  $D_4^{25} = 1.40$ ,  $n_D^{25} = 1.5758$  (20S), accompanied by chlorobenzene (3:7903),  $CO_2$ , and under certain conditions by hexachloroethane (3:4835).]

[ $\bar{C}$  with large excess  $EtMgBr$  in boilg. ether evolves ethylene and on subsequent treatment with aq. gives a mixt. of ethylene + acetylene; for explanation see (209). —  $\bar{C}$  with  $n$ -butyllithium in pet. eth. gives violent explosion (210).]

[For study of reactn. of  $\bar{C}$  with pyridine or piperidine at 16–18° see (211).]

Ⓢ Color test with  $NH_4OH/Cu_2Cl_2$ :  $\bar{C}$  (1–2 drops) in small glass-stoppered bottle filled with conc. aq.  $NH_4OH$ , treated with powdered  $Cu_2Cl_2$ , stopper quickly inserted (to force out air and excess liquid), shaken, and allowed to stand, gives in 3 days a pale amethyst color (212); note, however, that  $\bar{C}$  on stdg. with metallic  $Cu$  + conc. aq.  $NH_4OH$  develops rich port-wine red color in aq. layer and brown coating on the copper (213). — Note also that neither of these tests should be regarded as conclusive (see (212) (213)).

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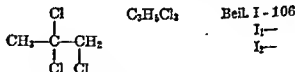
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## 3:5475 1,2,2-TRICHLOROPROPANE



B.P. 123° (1) (2)  
123-125° (3)

 $D_{25}^{25} = 1.318$ 

[For prepn. as a by-product of the chlorination of propane see (2); for formn. of  $\bar{C}$  (47%) in chlorination of 1,2-dichloropropane (3:5200) see (3).]

$\bar{C}$  with alc. KOH splits out HCl and gives two stereoisomeric 1,2-dichloropropenes, viz., 3:5110 and 3:5150.

3:5475 (1) Herzfelder, *Ber.* 26, 2435 (1893). (2) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,073, June 4, 1935; *Cent.* 1935, I 1500. (3) Zellner (to Tide Water Associated Oil Co.), U.S. 2,370,342, Feb. 27, 1945, *C.A.* 39, 3534 (1945).

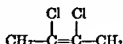
# CHAPTER XIII

## DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

### Section 1. $D_4^{20}$ greater than 1.1500

(3:5500-3:5999)

3:5500 *cis*-2,3-DICHLOROBUTENE-2  $\text{C}_4\text{H}_6\text{Cl}_2$  Beil. S.N. 11



B.P. 124-126° at 758 mm. (1)

$D_4^{20} = 1.1618$  (1)  $n_D^{20} = 1.4590$  (1)  
 $D_4^{18} = 1.1620$  (1)  $n_D^{18} = 1.4616$  (1)

[See also *trans* stereoisomer (3:7395).]

[For prepn. of  $\bar{C}$  (accompanied by its *trans* stereoisomer (3:7395)) from 2,2,3-trichlorobutane (3:5680) with solid KOH (1 mole) at 135-140° see (1).]

$\bar{C}$  on oxdn. with 3% aq.  $\text{KMnO}_4$  yields (1) acetic acid (1:1010).

$\bar{C}$  in  $\text{CCl}_4$  at -20° treated with 7%  $\text{O}_3$ , then hydrolyzed, yields (1) acetic acid (1:1010) + acetaldehyde (1:0100).

3:5500 (1) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 6, 1553-1558 (1936); *Cent.* 1937, I 3785; *C.A.* 31, 2165 (1937).

3:5515 TRICHLOROMETHYLENE CARBOXYMATE  $\text{C}_2\text{O}_2\text{Cl}_4$  Beil. III - 18  
 $\text{2 O.CO.Cl}$  III<sub>1</sub>-(8)  
III<sub>2</sub>-(16)

B.P.		M.P.			
127.5-128°	(1) cor. (2)	-57°	$D_{21}^{21} = 1.632$	(7)	$n_D^{26} = 1.456$ (1)
127°	at 760 mm. (3)				
126-127°	at 745 mm. (4)		$D_{15}^{15} = 1.655$	(3)	$n_D^{22} = 1.45664$ (8)
	(5)				
127.2°	at 725 mm. (6)				
49°	at 50 mm. (3)				
45°	at 26 mm. (7)				
20°	at 10.3 mm. (1)				
0°	at 2-4 mm. (1)				

Colorless oily liq. with irritating and suffocating odor, but (when pure) not especially lachrymatory. — Ord. samples may cont. triphosgene (3:1915).

[For prepn. from methyl formate (1:1000) or methyl chloroformate (3:5075) by chlorination see (8) (3) (9) (2) (1); for prepn. from *bis*-(trichloromethyl) carbonate (triphosgene) (3:1915) see (1); for German prepn. in World War I see (10).]

$\bar{C}$  (when pure) boils with no decompn. (1); however, above 300° (2) or on contact with activated carbon, charcoal, or iron oxide at ord. temp. (1)  $\bar{C}$  decomposes to phosgene

(3:5000). —  $\bar{C}$  on contact with alumina (1),  $AlCl_3$  (5), or  $FeCl_3$  (3) decomposes in a different mode yielding  $CCl_4$  (3:5100) +  $CO_2$ .

$\bar{C}$  with aq. hydrolyzes slowly in the cold but rapidly at  $100^\circ$  yielding only  $HCl$  +  $CO_2$  (1) (3);  $\bar{C}$  on warming with aq.  $Na_2CO_3$  yields  $NaCl$  +  $CO_2$  (3).

$\bar{C}$  on treatment at  $20^\circ$  for 5 min. with  $NaI$  in acetone evolves  $CO$  and separates  $I_2$  to 98.8% of amt. expressed by reaction:  $Cl_3C.O.CO.Cl + 2NaI \rightarrow 2CO + 4NaCl + I_2$  (11) [cf. chloromethyl chloroformate (3:5275), dichloromethyl chloroformate (3:5315), and triphosgene (3:1915)].

$\bar{C}$  with aq.  $NH_4OH$  reacts vigorously yielding urea +  $NH_4Cl$ . —  $\bar{C}$  with excess aniline in either aq. or non-aq. soln. is converted to  $N,N'$ -diphenylurea (carbanilide), m.p.  $233^\circ$ , + aniline hydrochloride (3). [Note that with insufficient aniline a mixt. of phenyl isocyanate +  $N$ -phenylcarbamyl chloride may form (3).]

$\bar{C}$  on addn. in cold to conc. soln. of phenol (1 mole) in aq.  $NaOH$  separates an oil (which soon solidifies) of phenyl trichloromethyl carbonate [Beil. VI<sub>1</sub>-(88)], ndls. from ether, m.p.  $70.5^\circ$  (12),  $66^\circ$  (3); this product upon warming with aq. sodium phenolate (or  $\bar{C}$  warmed with excess sodium phenolate in one operation) yields diphenyl carbonate (1:2335), cryst. from alc., m.p.  $78^\circ$  (12). [For corresponding reactions with  $p$ -cresol (1:1410),  $\beta$ -naphthol (1:1540),  $p$ -chlorophenol (3:0475), and  $p$ -nitrophenol see (13).]

$\bar{C}$  with pyridine yields a yel. double quaternary ammonium salt  $C_6H_5N(Cl).CO(Cl)-N.C_6H_5$  which by aq. is decomposed to pyridine hydrochloride +  $CO_2$  (14).

[For use of  $\bar{C}$  in prepn. of acid chlorides of carboxylic or sulfonic acids see (15); similarly  $\bar{C}$  htd. with anhydrous  $NaOAc$  gives  $Ac_2O$  +  $NaCl$  +  $CO_2$  (2); for actn. on methyl hydrogen sulfate yielding methyl chlorosulfonate + phosgene +  $CO_2$  see (16).]

[For use of  $\bar{C}$  for introduction of a second  $-CO.Cl$  group into acid chlorides see (17).]

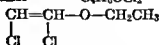
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### 3:5540 $\alpha,\beta$ -DICHLOROVINYL ETHYL ETHER



Beil. I - 724

( $\alpha,\beta$ -Dichloro- $\alpha$ -ethoxyethylene)



I<sub>1</sub>-(377)

I<sub>2</sub>-(780)

B.P.  $128.2^\circ$  cor. (1)

$125-127^\circ$  (4)

$122-126^\circ$  (2)

$D_4^{25} = 1.1972$  (3)

$D_4^{20} = 1.2037$  (3)

$n_D^{16.5} = 1.45584$  (3)

$\bar{C}$  has the possibility of existing in two geometrically isomeric forms, but only this one has as yet been recognized.

[For prepn. of  $\bar{C}$  from trichloroethylene (3:5170) with alc.  $KOH$  (4), with alc.  $NaOEt$  (yield: 81% (5), 70% (2)), or with alc.  $NaOH$  +  $CaO$  (6) see indic. refs.; from 1,1,1,2-tetrachloroethane (3:5555) with  $NaOEt$  see (1).]

[ $\bar{C}$  with calcd. amt. aq. (7), or with conc.  $HCl$  (8) yields ethyl chloroacetate (3:5700);

$\bar{C}$  on boilg. with aq. to complete soln. yields (9) chloroacetic acid (3:1370);  $\bar{C}$  on htg. with aq. in s.t. at  $180^\circ$  yields (1) glycolic acid (1.0430), EtCl (3:7015) + HCl.]

[ $\bar{C}$  with HCl gas yields (10) an addn. prod. which on htg. decomposes to chloroacetyl chloride (3:5235) + EtCl (3:7015);  $\bar{C}$  with monobasic org. acids yields (2) on htg. ethyl chloroacetate (3:5700) + corresp. acid chloride; with succinic acid the products are (2) ethyl chloroacetate (3:5700) + succinic anhydride (1:0710).]

[ $\bar{C}$  with alcohols yields mainly (2) (11) the corresp. alkyl chloroacetate + EtCl (some ethyl chloroacetate + alkyl chloride are also formed (2));  $\bar{C}$  htd. with excess NaOEt yields (1) sodium salt of ethoxyacetic acid (1:1070).]

[ $\bar{C}$  with phenols yields exclusively (2) the corresp. aryl chloroacetate + EtCl; e.g.,  $\bar{C}$  with  $\beta$ -naphthol (1:1540) yields (2)  $\beta$ -naphthyl chloroacetate, m.p.  $95^\circ$  (2).]

$\bar{C}$  with aniline in aq. or aq. alc. soln. yields (12) ethyl *N*-phenylaminoacetate (90%) [Beil. XII-470, XII<sub>1</sub>-(263)], m.p.  $58^\circ$ , and phenylaminoacetanilide (10%) [Beil. XII-556, XII<sub>1</sub>-(285)], m.p.  $112^\circ$

[ $\bar{C}$  readily absorbs  $Cl_2$  at ord. temp.; if moisture is carefully excluded, the prod. breaks up (13) (14) on keeping or on htg. into dichloroacetyl chloride (3:5290) + EtCl (3:7015); if, however, moisture is given access or aq. added, then on keeping or htg. the prod. breaks up (13) (14) and on distn. gives alm. theoretical yield of ethyl dichloroacetate (3:5850) + HCl.]

[ $\bar{C}$  readily absorbs  $Br_2$ ; with complete exclusion of aq. the products are (13) (14) bromo-chloro-acetyl chloride, b.p.  $138-139^\circ$  (13), and EtBr; in pres. of aq. the products are ethyl chloro-bromo-acetate, b.p.  $174^\circ$ ,  $D_4^{22} = 1.5890$  (13), + HCl + HBr; some bromo-chloro-acetyl bromide, b.p.  $158-160^\circ$ ,  $47-49^\circ$  at 15 mm. (15), and  $C_2H_5Cl$  (3:7015) are also (15) formed. —  $\bar{C}$  on treatment with  $Br_2$  in the cold, then immediately followed by alc. KOH, gives good yield (3) of  $\beta$ -bromo- $\alpha,\beta$ -dichlorovinyl ethyl ether, b.p.  $177^\circ$  at 754 mm.,  $D_4^{20} = 1.6565$ ,  $n_D^{17} = 1.50427$  (3).]

[ $\bar{C}$  treated with ICl, stood 30 min. (17), filtered from  $I_2$ , then htd. to  $50^\circ$  to expel  $C_2H_5Cl$  gives (16) (17) chloro-iodo-acetyl chloride; addn. of aq. to latter yields by hydrolysis (16) (17) chloro-iodo-acetic acid, colorless lts from li. pet., m.p.  $90^\circ$  (16).]

3:5540 (1) Geuther, Brockhoff, *J. prakt. Chem.* (2) 7, 111-117 (1873). (2) Crompton, Vanderstichele, *J. Chem. Soc.* 117, 691-693 (1920). (3) Smith, *J. Chem. Soc.* 1927, 1099-1102. (4) Paterno, Oghaloro, *Ber.* 7, 80-81 (1874). (5) Stephens, *J. Soc. Chem. Ind.* 43, T313-314, 327-328 (1921); *Cent.* 1925, I 357. (6) Imbert, Consortium für Elektrochem. Ind., Ger. 216,940, Dec. 13, 1909, *Cent.* 1910, I 308. (7) Imbert, Consortium für Elektrochem. Ind., Ger. 209,268, April 27, 1909, *Cent.* 1909, I 1785. (8) Imbert, Consortium für Elektrochem. Ind., Ger. 210,502, June 7, 1909, *Cent.* 1909, II 78. (9) Imbert, Consortium für Elektrochem. Ind., Ger. 216,716; Nov. 30, 1909, *Cent.* 1910, I 214. (10) Consortium für Elektrochem. Ind., Ger. 222,194, May 19, 1910, *Cent.* 1910, I 1999.

(11) Imbert, Consortium für Elektrochem. Ind., Ger. 212,592, Sept. 6, 1909; *Cent.* 1909, I 1024. (12) Imbert, Consortium für Elektrochem. Ind., Ger. 109,624, June 24, 1908, *Cent.* 1908, II 358. (13) Crompton, Triffitt, *J. Chem. Soc.* 119, 1874-1875. (14) McKie, *J. Chem. Soc.* 123, 2213-2217 (1923). (15) Backer, Mook, *J. Chem. Soc.* 1928, 2126. (16) Crompton, Carter, *J. Chem. Soc.* 123, 576-577 (1923). (17) McMath, Read, *J. Chem. Soc.* 1927, 538-539.

<sup>23</sup> see (10). —  $\bar{C}$  with di-n-butyl ether (1:7553): for b.p., vapor-liq. equil., and  $D$  see (10). —  $\bar{C}$  with  $\beta,\beta'$ -dichloro-diethyl ether (3:6235): for b.p., vapor-liq. equil., and  $D$  see (10). (see below under azeotropes).

$\bar{C}$  with chlorinated hydrocarbons.  $\bar{C}$  with 1,2-dichloroethane (3:5150): for b.p., vapor-liq. equil., and  $D$  see (31) (see also note — (For use of ethylene dichloride in dehydration of  $\bar{C}$  see (32))

### AZEOTROPES CONTAINING $\bar{C}$

Binary azeotropes.  $\bar{C}$  with water forms a constant-boiling mixt. b.p. 55.3° (26) (8), 97.8° at 760 mm. (23) (32). contg. 45.8 wt. %  $\bar{C}$  (41) 51.5 wt. %  $\bar{C}$  (32)  $\bar{C}$ : constants for this azeotropic mixt. at other press. include the following: b.p. 96-96.2° (26); at 735 mm., b.p. = 95.5° (25) (11), contg. 51.5 wt. %  $\bar{C}$  at 504 mm., b.p. = 86.4° (23); at 430 mm., b.p. = 81.55°, contg. 49.2 wt. %  $\bar{C}$ . Note that compn. changes only slightly (25) with press. — For study of this (11) (23) or of HCl (11) see infra. refs.

$\bar{C}$  with toluene (1:7201) gives a constant-boiling mixt. b.p. 74.4°, contg. 68 mole %  $\bar{C}$  (10). —  $\bar{C}$  with di-n-butyl ether (1:7553) gives a constant-boiling mixt. b.p. 68 mole %  $\bar{C}$  (10). —  $\bar{C}$  with  $\beta,\beta'$ -dichloro-diethyl ether (3:6235) gives a constant-boiling mixt. b.p. 123.2°, contg. 91.8 mole %  $\bar{C}$  (10).

Ternary azeotropes:  $\bar{C}$  with aq. +  $C_6H_6$  (1:7430) gives a constant-boiling mixt. b.p. 67.0-67.3° (29). —  $\bar{C}$  with aq. + ethylene dichloride (3:6235) gives a constant-boiling mixt. b.p. 69.6° (29). —  $\bar{C}$  with aq. + 1,1,2-trichloroethane (3:6235) gives a constant-boiling mixt. b.p. 70.8-71.5° (29).

### MANIPULATORY PHYSICAL PROPERTIES OF $\bar{C}$

[For sepn. of  $\bar{C}$  from gas mixts. by adsorption (7) on  $Mg(ClO_4)_2$  see (34).]

### USES OF $\bar{C}$

The manifold uses of  $\bar{C}$ , based upon both its physical and its chemical properties, cannot here be reviewed in detail; however, some examples include the following:

[For use in sepn. of benzofuran from hydrocarbon mixts. (33), in demerolization of naphthenes from mineral lubricating oils (35), in refining of rosin (36) and pine lignin (38) (39), as solv. for various resins (37), as solv. for cellulose and cellulose ethers (42), for addn. to rayon spinning baths (43) see infra. refs.]

### PHYSIOLOGICAL AND BIOCHEM. BEHAVIOR OF $\bar{C}$

[For study of pharmacol. of  $\bar{C}$  (or its phosphoric esters, etc.) see (44), for poisoning by  $\bar{C}$  see (45) (46); for study of toxicity of vapor of  $\bar{C}$  see (45) (46).]

[For effect of  $\bar{C}$  upon amylase (47) (48) or lipase (49) see infra. refs.; for effect of  $\bar{C}$  of yeast of depressed enzymatic activity see (50).]

### DETERMINATION OF $\bar{C}$

[For colorimetric detn. of  $\bar{C}$  by reaction with diazotized sulfanilic acid in aq. soln. see (106) (note that method involves oxidn. of  $\bar{C}$  by the reagt. to chloroacetaldehyde (3:7212) and color forms with latter); for detn. of  $\bar{C}$  in aq. solns. by refractometry (11) (23) (32) (33) (34) (35) (36) (37) (38) (39) (40) (41) (42) (43) (44) (45) (46) (47) (48) (49) (50) (51) (52) (53) (54) (55) (56) (57) (58) (59) (60) (61) (62) (63) (64) (65) (66) (67) (68) (69) (70) (71) (72) (73) (74) (75) (76) (77) (78) (79) (80) (81) (82) (83) (84) (85) (86) (87) (88) (89) (90) (91) (92) (93) (94) (95) (96) (97) (98) (99) (100) (101) (102) (103) (104) (105) (106) (107) (108) (109) (110) (111) (112) (113) (114) (115) (116) (117) (118) (119) (120) (121) (122) (123) (124) (125) (126) (127) (128) (129) (130) (131) (132) (133) (134) (135) (136) (137) (138) (139) (140) (141) (142) (143) (144) (145) (146) (147) (148) (149) (150) (151) (152) (153) (154) (155) (156) (157) (158) (159) 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3:5552	2-CHLOROETHANOL-1 (Ethylene chlorohydrin, $\beta$ -chloroethanol, $\beta$ -chloroethyl alcohol, "glycol chlorohydrin")	$\text{CH}_2\text{--CH}_2\text{OH}$   Cl	$\text{C}_2\text{H}_5\text{OCl}$	Beil. I - 337 I <sub>1</sub> -(170) I <sub>2</sub> -(333)
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B.P.		F.P.		
[132°	at 761 mm. (1)]	-67.5° (7)	$D_4^{25} = 1.1972$ (14)	$n_D^{25} = 1.44123$ (22)
[132.0°	(2)]	(8)	1.19654 (8)	1.4412 (18)
[130-131°	at 760 mm. (3)]	-69.0°	1.1961 (10)	1.44012 (9)
		(21)	1.1947 (9)	
129.46°	at 761.1 mm. (4)			
128.7-128.8°	at 764 mm. (5)			
128.60°	at 760 mm. (6)			$n_D^{24} = 1.4402$ (10)
128.60°	at 760 mm. (7)			
128.6°	at 760 mm. (8)		$D_4^{20} = 1.2022$ (13)	$n_D^{20} = 1.44212$ (22)
128.1-128.2°	at 762 mm. (9)		1.20190 (8)	1.4421 (23)
128.05°	at 744 mm. (6)		1.20027 (6)	1.44208 (13)
128.0°	at 760 mm. (10)		1.1088 (4)	(9)
128°	(11)(12)		1.1081 (22)	1.44107 (6)
127.9-128.1°	at 761 mm. (13)			1.44189 (24)
127.9-128.1°	at 741 mm. (14)			1.44163 (25)
127.6-128.6°	(15)			
127.1-128.1°	cor. (16)		$D_4^{15} = 1.20720$ (13)	$n_D^{15} = 1.44382$ (22)
127-127.5°	(17)			1.44380 (8)
126.5-126.7°	at 729 mm. (18)			
51-52°	at 22 mm. (1)			
44°	at 20 mm. (19)			
43°	at 3-4 mm. (20)			

Colorless liq. — miscible with aq. (see also below) and most org. solv.

## MISCELLANEOUS PHYSICAL PROPERTIES

### BINARY SYSTEMS CONTAINING $\bar{C}$

$\bar{C}$  + water. For values of  $D_4^{20}$  and  $n_D^{20}$  (also  $n_D^{20}$ ,  $n_F^{20}$ ,  $n_D^{20}$ ) over whole range 0-100%  $\bar{C}$  see (5) cf. (22) (23); for thermal anal. of systems see (26). — For study of salting-out of  $\bar{C}$  from its aq. solns. (11) or its isolation by ether extraction of aq. solns. satd. with NaCl or  $\text{Na}_2\text{CO}_3$  (27) see indic. refs. — For concn. of  $\bar{C}$ , i.e., dehydration of its aq. solns. by distn. of the water with  $\text{C}_6\text{H}_6$  (28), with 1,2-dichloroethane (ethylene dichloride) (3:5130) (29), or with cyclohexanol (1:6415) (30) see indic. refs. — See also below under azeotropes.

Note that boilg. aq. solns. of  $\bar{C}$  undergo slow decompn., e.g., about 10% in 8 hrs. (23), 50% in 5 hrs. (107) cf. (11) (presumably by loss of HCl and evoln. of ethylene oxide (1:6105), b.p. 10.7°, and/or (38) acetaldehyde (1:0100), b.p. 20.2°.

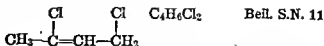
$\bar{C}$  with hydrocarbons.  $\bar{C}$  with  $\text{C}_6\text{H}_6$  (1:7400): for b.p., vapor-liq. equil., and  $n_D^{25}$  see (10). —  $\bar{C}$  with toluene (1:7405): for b.p., vapor-liq. equil., and  $n_D^{25}$  see (10) (see also below under azeotropes).

$\bar{C}$  with alcohols.  $\bar{C}$  with butanol-1 (1:6180): for b.p., vapor-liq. equil., and  $n_D^{25}$  see (10). —  $\bar{C}$  with isobutyl alc. (1:6165): for b.p., vapor-liq. equil., and  $n_D^{25}$  see (10).

$\bar{C}$  with ethers.  $\bar{C}$  with di-isopropyl ether (1:6125): for b.p., vapor-liq. equil., and



3:5550 1,3-DICHLOROBUTENE-2  
(2,4-Dichlorobutene-2)



B.P. 127-129°	at 756 mm. (1)	$D_4^{20} \div 1.1591$ (1) (3)	$n_D^{20} = 1.47239$ (1)
127-128.5°	at 753 mm. (2)	1.1582 (2)	1.4695 (2)
61-63°	at 70 mm. (1)		
56-57°	at 55 mm. (3)		$n_D^{20} = 1.46988$ (1)
53-54°	at 55 mm. (2)		1.4694 (3)
53-54°	at 50 mm. (1)		

Colorless liq. with characteristic odor (1). —  $\bar{C}$  is formed (5-10% (4) (5) (11)) cf. (10) in synthesis of chloroprene (3:7080). — [For use in mfg. of unsatd. cellulose ethers see (6); in mfg. of unsatd. ethers of alcohols and phenols for use as solvents, disinfectants, etc., see (7) (8).]

[For prepn. of  $\bar{C}$  readily and in quantity (1) from vinylacetylene by shaking with an excess (4 moles) of HCl contg. CuCl see (1); from methyl vinyl ketone in 33% yield (together with other products) with PCl<sub>5</sub> at -10° see (2), from 2-chlorobutene-2 (3:7105) (together with other products) by actn. of Cl<sub>2</sub> at 350° see (9); for formn. of  $\bar{C}$  (together with other products) from trimethylethylene + Cl<sub>2</sub> see (11).]

$\bar{C}$  passed over silica gel or clay at 245-275° loses HCl yielding (4) 17-18% 3-chlorobutadiene-1,3 ("Chloroprene") (3:7080).

$\bar{C}$  on hydrolysis with steam (12), or aq. alk. (5) (12), or aq. K<sub>2</sub>CO<sub>3</sub> (2), aq. Na<sub>2</sub>CO<sub>3</sub> (70-80% yield (4)) or CaCO<sub>3</sub> (3) gives 3-chlorobuten-2-ol-1 (3:8207) q.v., b.p. 161-162°. — [Note that  $\bar{C}$  with alc. alk. does not hydrolyze or lose HCl but instead gives the corresp. ethers (see details under 3-chlorobuten-2-ol-1 (3:8207)).]

$\bar{C}$  with Cl<sub>2</sub> yields (13) (14) (15) a mixt. of 2,3,4-trichlorobutene-1 (3:9064), 1,2,3,3-tetrachlorobutane (3:9080), and 1,2,2,3,4-pentachlorobutane (3:9070).

35550 (1) Carothers, Berchet, Collins, *J. Am. Chem. Soc.* 54, 4066-4070 (1932). (2) Churbakov, *J. Gen. Chem. (U.S.S.R.)* 10, 977-980 (1940); *C.A.* 35, 2469 (1941). (3) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 7, 658-662 (1937); *Cent.* 1937, II 371; *C.A.* 31, 5754 (1937). (4) Klebanaskii, *ibid.* (1936). (5) *ibid.* 6; *Cent.* 1937, II 383-408 (1935).

(7) Berchet (to du Pont), U.S. 2,079,758, May 11, 1937; *Cent.* 1937, II 2597; *C.A.* 31, 4676 (1937).

(8) Deichsel (to I.G.), Brit. 443,113, Feb. 20, 1936; *Cent.* 1937, I 383-384; *C.A.* 30, 4873 (1936).

(9) N. V. de Bataafsche Petroleum Maatschappij, Brit. 468,016, June 28, 1937; French 810,112, Mar. 15, 1937; *Cent.* 1937, II 4102; *C.A.* 31, 8543 (1937). (10) du Pont Co., Brit. 395,131, Aug. 3, 1933; *Cent.* 1933, 2455; Brit. 387,325; *Cent.* 1933, I 4525; French 721,532, Mar. 4, 1932; *Cent.* 1932, II 2107.

(11) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 7, 658-662 (1937); *Cent.* 1937, II 371; *C.A.* 31, 5754 (1937). (12) *ibid.* 6; *Cent.* 1937, II 383-408 (1935). (13) *ibid.* 6; *Cent.* 1937, II 383-408 (1935). (14) *ibid.* 6; *Cent.* 1937, II 383-408 (1935). (15) Coffman (to du Pont), *ibid.* 6; *Cent.* 1937, II 383-408 (1935). (16) Carothers, Berchet, Collins, *J. Am. Chem. Soc.* 54, 4066-4070 (1932). (17) *ibid.* 54, 4070-4071 (1932). (18) *ibid.* 54, 4071-4072 (1932). (19) *ibid.* 54, 4072-4073 (1932). (20) *ibid.* 54, 4073-4074 (1932). (21) *ibid.* 54, 4074-4075 (1932). (22) *ibid.* 54, 4075-4076 (1932). (23) *ibid.* 54, 4076-4077 (1932). (24) *ibid.* 54, 4077-4078 (1932). (25) *ibid.* 54, 4078-4079 (1932). (26) *ibid.* 54, 4079-4080 (1932). (27) *ibid.* 54, 4080-4081 (1932). (28) *ibid.* 54, 4081-4082 (1932). (29) *ibid.* 54, 4082-4083 (1932). (30) *ibid.* 54, 4083-4084 (1932). (31) *ibid.* 54, 4084-4085 (1932). (32) *ibid.* 54, 4085-4086 (1932). (33) *ibid.* 54, 4086-4087 (1932). (34) *ibid.* 54, 4087-4088 (1932). (35) *ibid.* 54, 4088-4089 (1932). (36) *ibid.* 54, 4089-4090 (1932). (37) *ibid.* 54, 4090-4091 (1932). (38) *ibid.* 54, 4091-4092 (1932). (39) *ibid.* 54, 4092-4093 (1932). (40) *ibid.* 54, 4093-4094 (1932). (41) *ibid.* 54, 4094-4095 (1932). (42) *ibid.* 54, 4095-4096 (1932). (43) *ibid.* 54, 4096-4097 (1932). (44) *ibid.* 54, 4097-4098 (1932). (45) *ibid.* 54, 4098-4099 (1932). (46) *ibid.* 54, 4099-4100 (1932). (47) *ibid.* 54, 4100-4101 (1932). (48) *ibid.* 54, 4101-4102 (1932). (49) *ibid.* 54, 4102-4103 (1932). (50) *ibid.* 54, 4103-4104 (1932). (51) *ibid.* 54, 4104-4105 (1932). (52) *ibid.* 54, 4105-4106 (1932). (53) *ibid.* 54, 4106-4107 (1932). (54) *ibid.* 54, 4107-4108 (1932). (55) *ibid.* 54, 4108-4109 (1932). (56) *ibid.* 54, 4109-4110 (1932). (57) *ibid.* 54, 4110-4111 (1932). (58) *ibid.* 54, 4111-4112 (1932). (59) *ibid.* 54, 4112-4113 (1932). (60) *ibid.* 54, 4113-4114 (1932). (61) *ibid.* 54, 4114-4115 (1932). (62) *ibid.* 54, 4115-4116 (1932). (63) *ibid.* 54, 4116-4117 (1932). (64) *ibid.* 54, 4117-4118 (1932). (65) *ibid.* 54, 4118-4119 (1932). (66) *ibid.* 54, 4119-4120 (1932). (67) *ibid.* 54, 4120-4121 (1932). (68) *ibid.* 54, 4121-4122 (1932). (69) *ibid.* 54, 4122-4123 (1932). (70) *ibid.* 54, 4123-4124 (1932). (71) *ibid.* 54, 4124-4125 (1932). (72) *ibid.* 54, 4125-4126 (1932). (73) *ibid.* 54, 4126-4127 (1932). (74) *ibid.* 54, 4127-4128 (1932). (75) *ibid.* 54, 4128-4129 (1932). (76) *ibid.* 54, 4129-4130 (1932). (77) *ibid.* 54, 4130-4131 (1932). (78) *ibid.* 54, 4131-4132 (1932). (79) *ibid.* 54, 4132-4133 (1932). (80) *ibid.* 54, 4133-4134 (1932). (81) *ibid.* 54, 4134-4135 (1932). (82) *ibid.* 54, 4135-4136 (1932). (83) *ibid.* 54, 4136-4137 (1932). (84) *ibid.* 54, 4137-4138 (1932). (85) *ibid.* 54, 4138-4139 (1932). (86) *ibid.* 54, 4139-4140 (1932). (87) *ibid.* 54, 4140-4141 (1932). (88) *ibid.* 54, 4141-4142 (1932). (89) *ibid.* 54, 4142-4143 (1932). (90) *ibid.* 54, 4143-4144 (1932). (91) *ibid.* 54, 4144-4145 (1932). (92) *ibid.* 54, 4145-4146 (1932). (93) *ibid.* 54, 4146-4147 (1932). (94) *ibid.* 54, 4147-4148 (1932). (95) *ibid.* 54, 4148-4149 (1932). (96) *ibid.* 54, 4149-4150 (1932). (97) *ibid.* 54, 4150-4151 (1932). (98) *ibid.* 54, 4151-4152 (1932). (99) *ibid.* 54, 4152-4153 (1932). (100) *ibid.* 54, 4153-4154 (1932).

3:5552	2-CHLOROETHANOL-1 (Ethylene chlorohydrin, $\beta$ -chloroethanol, $\beta$ -chloroethyl alcohol, "glycol chlorohydrin")	$\text{CH}_2\text{—CH}_2\text{OH}$ $\text{Cl}$	$\text{C}_2\text{H}_4\text{OCl}$	Beil. I - 337 I <sub>1</sub> -(170) I <sub>2</sub> -(333)
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B.P.		F.P.			
[132°	at 761 mm.	(1)]	-67.5° (7)	$D_4^{25} = 1.1972$ (14)	$n_D^{25} = 1.44123$ (22)
[132.0°		(2)]	(8)	1.19654 (8)	1.4412 (18)
[130-131°	at 760 mm.	(3)]	-69.0°	1.1061 (10)	1.44012 (9)
			(21)	1.1047 (9)	
129.46°	at 761.1 mm.	(4)			
128.7-128.8°	at 764 mm.	(5)			$n_D^{24} = 1.4402$ (10)
128.66°	at 760 mm.	(6)			
128.60°	at 760 mm.	(7)			
128.6°	at 760 mm.	(8)		$D_4^{20} = 1.2022$ (13)	$n_D^{20} = 1.44212$ (22)
128.1-128.2°	at 762 mm.	(9)		1.20100 (8)	1.4421 (23)
128.05°	at 744 mm.	(6)		1.20027 (6)	1.44208 (13)
128.0°	at 760 mm.	(10)		1.1988 (4)	(9)
128°	(11)(12)			1.1081 (22)	1.44197 (6)
127.9-128.1°	at 761 mm.	(13)			1.44189 (24)
127.9-128.1°	at 741 mm.	(14)			1.44163 (25)
127.6-128.0°		(15)			
127.1-128.1°	cor.	(16)		$D_4^{15} = 1.20720$ (13)	$n_D^{15} = 1.44382$ (22)
127-127.5°		(17)			1.44380 (8)
120.5-126.7°	at 729 mm.	(18)			
51-52°	at 22 mm.	(1)			
44°	at 20 mm.	(19)			
43°	at 3-4 mm.	(20)			

Colorless liq. — miscible with aq. (see also below) and most org. solv.

## MISCELLANEOUS PHYSICAL PROPERTIES

### BINARY SYSTEMS CONTAINING $\bar{\text{C}}$

$\bar{\text{C}}$  + water. For values of  $D_4^{20}$  and  $n_D^{20}$  (also  $n_D^{20}$ ,  $n_D^{20}$ ,  $n_D^{20}$ ) over whole range 0-100%  $\bar{\text{C}}$  see (6) cf (22) (23); for thermal anal. of systems see (26). — For study of salting-out of  $\bar{\text{C}}$  from its aq. solns. (11) or its isolation by ether extraction of aq. solns. satd. with NaCl or  $\text{Na}_2\text{CO}_3$  (27) see indic. refs. — For concn. of  $\bar{\text{C}}$ , i.e., dehydration of its aq. solns. by distn. of the water with  $\text{C}_6\text{H}_6$  (28), with 1,2-dichloroethane (ethylene dichloride) (3:5130) (29), or with cyclohexanol (1:6415) (30) see indic. refs. — See also below under azeotropes.

Note that boilg. aq. solns. of  $\bar{\text{C}}$  undergo slow decompn., e.g., about 10% in 8 hrs. (23), 50% in 5 hrs. (107) cf (11) (presumably by loss of HCl and evoln. of ethylene oxide (1:6105), b.p. 10.7°, and/or (38) acetaldehyde (1:0100), b.p. 20.2°.

$\bar{\text{C}}$  with hydrocarbons.  $\bar{\text{C}}$  with  $\text{C}_6\text{H}_6$  (1:7400): for b.p., vapor-liq. equil., and  $n_D^{25}$  see (10). —  $\bar{\text{C}}$  with toluene (1:7405): for b.p., vapor-liq. equil., and  $n_D^{25}$  see (10) (see also below under azeotropes).

$\bar{\text{C}}$  with alcohols.  $\bar{\text{C}}$  with butanol-1 (1:6180): for b.p., vapor-liq. equil., and  $n_D^{25}$  see (10). —  $\bar{\text{C}}$  with isobutyl alc. (1:6165): for b.p., vapor-liq. equil., and  $n_D^{25}$  see (10).

$\bar{\text{C}}$  with ethers.  $\bar{\text{C}}$  with di-isopropyl ether (1:6125): for b.p., vapor-liq. equil., and

$n_D^{25}$  see (10). —  $\bar{C}$  with *di-n-butyl ether* (1:7950): for b.p., vapor-liq. equil., and  $n_D^{25}$  see (10). —  $\bar{C}$  with  $\beta,\beta'$ -dichloro-diethyl ether (3:6025): for b.p., vapor-liq. equil., and  $n_D^{25}$  see (10) (see below under azeotropes).

$\bar{C}$  with chlorinated hydrocarbons.  $\bar{C}$  with 1,2-dichloroethane (ethylene dichloride) (3:5130): for b.p., vapor-liq. equil., and  $D$  see (31) (see also below under azeotropes). (For use of ethylene dichloride in dehydration of  $\bar{C}$  see (30).)

#### AZEOTROPES CONTAINING $\bar{C}$

Binary azeotropes.  $\bar{C}$  with water forms a const.-boilg. mixt., b.p. 97.85° nt 760 mm. (26) (8), 97.8° at 760 mm. (23) (32), contg. 45.8 wt. % (8), 43.5 wt. % = 14.7 mole % (32)  $\bar{C}$ : constants for this azeotropic mixt. at other press. include the following: at 771 mm., b.p. 96-96.2° (26); at 735 mm., b.p. = 95.8° (33) (11), contg. 42.5 wt. %  $\bar{C}$  (33) (11); at 504 mm., b.p. = 86.4° (23); at 400 mm., b.p. = 80.55°, contg. 40.5 wt. %  $\bar{C}$  (23). — Note that compn. changes only slightly (23) with press. — For study of influence of NaCl (11) (23) or of HCl (11) see indic. refs.

$\bar{C}$  with toluene (1:7405) gives a const.-boilg. mixt., b.p. 106.9°, contg. 27 mole %  $\bar{C}$  (10). —  $\bar{C}$  with *di-n-butyl ether* (1:7950) gives a const.-boilg. mixt., b.p. 123.0°, contg. 68 mole %  $\bar{C}$  (10). —  $\bar{C}$  with  $\beta,\beta'$ -dichlorodiethyl ether (3:6025) gives a const.-boilg. mixt., b.p. 123.2°, contg. 91.8 mole %  $\bar{C}$  (10).

Ternary azeotropes:  $\bar{C}$  with aq. +  $C_6H_6$  (1:7400) gives a const.-boilg. mixt., b.p. 67.0-67.3° (20). —  $\bar{C}$  with aq. + ethylene dichloride (3:5130) gives a const.-boilg. mixt., b.p. 69.6° (29). —  $\bar{C}$  with aq. + 1,1,2-trichloroethylene (3:5170) gives a const.-boilg. mixt., b.p. 70.8-71.5° (29).

#### MISCELLANEOUS PHYSICAL PROPERTIES OF $\bar{C}$

[For sepn. of  $\bar{C}$  from gas mixts. by adsorption (?) on  $Mg(ClO_4)_2$  or other perchlorates see (34).]

#### USES OF $\bar{C}$

The manifold uses of  $\bar{C}$ , based upon both its physical and its chemical characteristics, cannot here be reviewed in detail; however, some examples include the following.

[For use in sepn. of butadiene from hydrocarbon mixts. (35), in dewaxing and removing naphthenes from mineral lubricating oils (36), in refining of rosin (37), in extraction of pine lignin (38) (39), as solv. for various resins (40), as solv. for cellulose acetate (41) or cellulose ethers (42), for addn. to rayon spinning baths (43) see indic. refs.]

#### PHYSIOLOGICAL AND BIOCHEM. BEHAVIOR OF $\bar{C}$

[For study of pharmacol. of  $\bar{C}$  (or its phosphoric esters, etc.) see (44); for reports of poisoning by  $\bar{C}$  see (45) (46); for study of toxicity of vapor of  $\bar{C}$  see (403).]

[For effect of  $\bar{C}$  upon amylase (47) (48) or lipase (49) see indic. refs.; for use of  $\bar{C}$  in prod. of yeast of depressed enzymatic activity see (50).]

#### DETERMINATION OF $\bar{C}$

[For colorimetric detn. of  $\bar{C}$  by reactn. with diazotized sulfanilic acid in alk. soln. at 25° see (106) (note that method involves oxidn. of  $\bar{C}$  by the reagt. to chloroacetaldehyde (3:7212) and color formn. with latter); for detn. of  $\bar{C}$  in aq. solns. by refractometry see (11) (25) (6) (23).]

PREPARATION OF  $\bar{C}$ 

From ethylene. With hypochlorous acid, e.g., from  $Cl_2 + aq.$  —  $\bar{C}$  is usually prepd. from ethylene by addn. of HOCl; the HOCl may be obtained by use of  $Cl_2 + aq.$  (sometimes in the pres. of alk. acceptors for the simultaneously formed HCl), by use of organic hypochlorites, or other org. cpds. which hydrolyze to give HOCl.

[For scientific papers discussing prepn. of  $\bar{C}$  from ethylene + HOCl ( $Cl_2 + aq.$ ) see (401) (11) (51) (52) (53) (54) (55) (56) (57) (58) (59); for very old work see (60); for examples of patents employing this method see citations (61)–(82) cf. (402), inclusive; for study of metal-corrosion problems involved in this method of prepn. of  $\bar{C}$  see (83).]

With organic hypochlorites (e.g., *ter*-butyl hypochlorite (3:7165)). [For patents on prepn. of  $\bar{C}$  from ethylene + *ter*-butyl hypochlorite see (84) (85).]

With *N*-chlorourea. [For prepn. of  $\bar{C}$  from ethylene with *N*-chlorourea in 5%  $H_2SO_4$  contg.  $CuCl_2$  at  $0^\circ$  (yield: 60–70%  $\bar{C}$  accompanied by 2% ethylene dichloride (3:5130)) see (86).]

From ethylene glycol (1:6465). [For prepn. of  $\bar{C}$  from ethylene glycol satd. with HCl gas and htd. in s.t. (12) (90), or treated at  $160^\circ$  (87) (4) or  $180^\circ$  (88) with stream of HCl (yields: 70–80% (88), 60% (87)), see indie. refs.; note that ethylene glycol with excess conc. HCl in s.t. at  $100^\circ$  gives no  $\bar{C}$  (89) but only ethylene dichloride (3:5130), while mere distn. with conc. HCl (9 moles) gives (15) only 12%  $\bar{C}$ .)]

[For prepn. of  $\bar{C}$  from ethylene glycol with  $S_2Cl_2$  (2.5 wt. pts. (91)) on refluxing (yields: 82.5% (92), 72.8% (91)) (93) (94) (95) see indie. refs.; for formn. of  $\bar{C}$  from glycol with  $SiCl_4$  see (96).]

From ethylene glycol esters. [For patents on prepn. of  $\bar{C}$  from ethylene glycol diformate (1:3402) with HCl gas at  $100^\circ$  via formn. of  $\beta$ -chloroethyl formate and subsequent alcoholysis of latter with MeOH/HCl (97), or from ethylene glycol diacetate (1:3511) with EtOH + HCl at  $125$ – $135^\circ$  under press. (EtOAc is also formed) (98), see indie. refs.]

From ethylene oxide (1:6106). [For formn. of  $\bar{C}$  from ethylene oxide with liq. HCl (99) or with  $S_2Cl_2$  (100) (other prods. are also formed) see indie. refs.]

From other miscellaneous sources. [For formn. of  $\bar{C}$  from 1,2-dichloroethane (ethylene dichloride) (3:5130) by conversion with  $SO_3$  below  $45^\circ$  to  $\beta$ -chloroethyl chlorosulfonate (see below) and subsequent hydrolysis to  $\bar{C}$  (101); from *bis*-( $\beta$ -chloroethyl) sulfate (see below) by refluxing with aq. (102); from  $\beta$ -chloroethyl trichloroacetate (3:6410) by shaking with aq. (103); from  $\beta$ -chloroethyl vinyl ether (3:7464) on distn. with aq. + trace of HCl (acetaldehyde is also formed) (104); from chloroacetaldehyde (3:7212) by reduction of carbonyl group with EtOMgBr (105) see indie. refs.]

CHEMICAL BEHAVIOR OF  $\bar{C}$ 

Pyrolysis of  $\bar{C}$ . [ $\bar{C}$  in s.t. at  $184^\circ$  for 10 hrs. yields (107) 1,2-dichloroethane (ethylene dichloride) (3:5130) and acetaldehyde (1:0100) (the latter partially as aldehyde resin); for study of rate of decompn. of  $\bar{C}$  at  $365^\circ$  see (108).]

## BEHAVIOR WITH INORGANIC REACTANTS

Reduction of  $\bar{C}$ . [ $\bar{C}$  with Na/Hg + aq. (109), or  $\bar{C}$  in aq. soln. in pres. of alk. with  $H_2$  at atm. press. + cat. (110), yields ethyl alcohol (1:6130); in latter method reduction is facilitated by NaOH, less so by  $Ca(OH)_2$  or  $CaCO_3$ ; using Pd/ $CaCO_3$  yield of EtOH is 91%; using Ni yield of EtOH is 80% accompanied by 20% ethylene glycol (1:6465) (110).]

Oxidation of  $\bar{C}$ .  $\bar{C}$  on oxidn. with  $CrO_3$  yields (111) chloroacetic acid (3:1370).

Behavior with  $\text{H}_2\text{O}$ .  $\bar{\text{C}}$  on boilg. with aq. undergoes gradual decomposition: e.g., 10% in 8 hrs. (23), 50% in 5 hrs. (107) cf. (11), presumably by loss of  $\text{HCl}$  and formation of ethylene oxide (1:6105), acetaldehyde (1:0100) etc. — [Note that  $\bar{\text{C}}$  with aq. vapor over  $\text{ZnCl}_2 + \text{ZnO}$  at 250–255° yields (112) acetaldehyde (1:0100).]

Behavior with inorganic acids. (See also below under behavior with salts of inorganic acids.)

With  $\text{H}_2\text{SO}_4$ .  $\bar{\text{C}}$  with conc.  $\text{H}_2\text{SO}_4$  readily dissolves and according to conditions yields either  $\beta$ -chloroethyl hydrogen sulfate or *bis*-( $\beta$ -chloroethyl) ether. (Note that  $\bar{\text{C}}$  with  $\text{SO}_2\text{Cl}_2$  (see below) gives *bis*-( $\beta$ -chloroethyl) sulfate.)

[For study of rate and extent of formn. of  $\beta$ -chloroethyl  $\text{HSO}_4$  with conc. or fuming  $\text{H}_2\text{SO}_4$  at 25° see (14); for reactn. of harium salt of this prod. with aniline see (113).]

$\bar{\text{C}}$  with conc.  $\text{H}_2\text{SO}_4$  (17% by wt. of  $\bar{\text{C}}$ ) refluxed 6 hrs. gives (114) *bis*-( $\beta$ -chloroethyl) ether (3:6025).

With  $\text{HNO}_3$ .  $\bar{\text{C}}$  with  $\text{HNO}_3/\text{H}_2\text{SO}_4$  (115) (116) gives (92% yield (115))  $\beta$ -chloroethyl nitrate,  $\text{ClCH}_2\text{CH}_2\text{ONO}_2$ , h.p. 149–150°; for use of this prod. in explosives see (115) (117); for use as ignition accelerator in Diesel engine fuels see (118) (119) (120).]

With  $\text{HNO}_2$ .  $\bar{\text{C}}$  with  $\text{HNO}_2$  (from  $\text{NaNO}_2 + \text{HCl}$ ) at  $-5^\circ$  gives (70% yield (121)) (122) (123)  $\beta$ -chloroethyl nitrite  $\text{ClCH}_2\text{CH}_2\text{ONO}$ , b.p. 90–91° (121), 89–89.5° (122),  $D_4^{20} = 1.212$  (122),  $n_D^{20} = 1.4125$  (122). (This prod. is not to be confused with the isomeric chloro-nitro-ethanes Beil. I-101.)]

Behavior with salts of inorganic acids. (For behavior with  $\text{NaCN}$ , anhyd.  $\text{Na}_2\text{CO}_3$ ,  $\text{NaSCN}$ , etc., see further below under organic reactants; for behavior with  $\text{NaSH}$  see further below under alkali reactants.)

With alkali iodides.  $\bar{\text{C}}$  with  $\text{NaI}$  in hot alc. (124) (125) or boiling acetone (126) for 16 hrs. (127) (better 4 hrs. (20)), or with  $\text{KI}$  in alc. at room temp. for 24 hrs. (128) gives (95% yield (127))  $\beta$ -iodoethanol (ethylene glycol iodohydrin), b.p. 176–177° dec. (124), 86–87° at 25 mm. (20), 85–88° at 25 mm. (127), 85° at 25 mm. (124), 61° at 7 mm. (4),  $D_4^{20} = 2.1968$  (4),  $n_D^{20} = 1.57134$  (24). [For study of rate of reaction of  $\bar{\text{C}}$  with  $\text{KI}$  in dry acetone at 50° and 60° see (16).]

With alkali sulfides (for alkali sulfhydrates, e.g.,  $\text{NaSH}$ , see below). — [ $\bar{\text{C}}$  with aq.  $\text{K}_2\text{S}$  (129) or with aq.  $\text{Na}_2\text{S}$  (11) (130) (131) (132) at 30–35° for 1 hr. (33) splits out 2  $\text{NaCl}$  giving (yields: 90–95% (11), 79–86% (33)) *bis*-( $\beta$ -hydroxyethyl) sulfide (“thiodiglycol”) [Beil. I-470, I<sub>1</sub>-(244), I<sub>2</sub>-(525)], b.p. 164–166° at 20 mm (33), 130° at 2 mm. (131), 104° at 0.005 mm. (132), f.p. =  $-16^\circ$  (132),  $D_4^{20} = 1.1821$  (132), 1.1819 (132),  $n_D^{20} = 1.52031$  (132), misc. with aq., readily sol. alc., acetone,  $\text{EtOAc}$ , or  $\text{CHCl}_3$ , but spar. sol. ether,  $\text{C}_6\text{H}_6$ , or  $\text{CCl}_4$  (131) (corresp. dibenzoate, m.p. 65° (133), di-(*p*-nitrobenzoate), m.p. 107.7° (134), *bis*-(*N*-phenylcarbamate), m.p. 128.5–129.5° (131)). — Note that this prod. (“thiodiglycol”) with  $\bar{\text{C}}$  at 100° for 13 hrs. (131) adds to form *tris*-( $\beta$ -hydroxyethyl)sulfonium chloride  $(\text{HOCH}_2\text{CH}_2)_3\text{SCl}$ , non-hygroscopic ndls., m.p. 126–127° (132), 125–126° (131). Note also that  $\bar{\text{C}}$  (1 mole) +  $\text{Na}_2\text{S}$  + 1-chloropropanol-2 (propylene chlorohydrin) (3:7747) yields (135) a mixed deriv., viz.,  $\beta$ -hydroxyethyl  $\beta$ -hydroxy-*n*-propyl sulfide.]

With alkali selenide.  $\bar{\text{C}}$  with aq.  $\text{Na}_2\text{Se}$  yields (136) *bis*-( $\beta$ -hydroxyethyl) selenide.]

With alkali disulfide.  $\bar{\text{C}}$  with aq.  $\text{Na}_2\text{S}_2 + \text{S}$  gives (46% yield (137)) (138) *bis*-( $\beta$ -hydroxyethyl) disulfide [Beil. I-471, I<sub>2</sub>-(528)], h.p. 155° at 30 mm.,  $D_4^{20} = 1.3375$  (137).]

With  $\text{NaHSO}_3$ .  $\bar{\text{C}}$  with solid  $\text{NaHSO}_3$  in a.t. at 170–180° for several hrs. gives (139) the salt of 2-hydroxyethanesulfonic acid-1 (“isethionic acid”).]

With  $\text{Na}_3\text{PO}_4$ .  $\bar{\text{C}}$  with satd. aq.  $\text{Na}_3\text{PO}_4$  as directed (140) cf. (3) gives (30% yield (140)) di-sodium  $\beta$ -hydroxyethyl phosphate, *cryst.* from aq. alc. as hexahydrate, m.p. 61° (140).]

With  $\text{Na}_3\text{AsO}_3$ .  $\bar{\text{C}}$  with aq. alk.  $\text{Na}_3\text{AsO}_3$  (from  $\text{As}_2\text{O}_3$  in aq. alk.) as directed (141) (142) (143) cf. (144) (145) gives  $\beta$ -hydroxyethylarsonic acid (also known as  $\beta$ -hydroxyethylarsinic acid) =  $\text{HOCH}_2\text{CH}_2\text{AsO}(\text{OH})_2$ , very sol. aq. but forming spar. sol. monohydrated calcium salt (141)]

With  $\text{Na}_2\text{SnO}_3$ .  $\bar{\text{C}}$  with aq. alk.  $\text{Na}_2\text{SnO}_3$  (from  $\text{SnCl}_2 + \text{aq. NaOH}$ ) gives (146) salt of  $\beta$ -hydroxyethylstannonic acid =  $\text{HOCH}_2\text{CH}_2\text{SnO}(\text{OH})_2$ .

Behavior with acid halides of inorganic acids. With thionyl chloride ( $\text{SOCl}_2$ ).  $\bar{\text{C}}$  with  $\text{SOCl}_2$  (small excess) in cold gives (83% yield (147))  $\beta$ -chloroethylsulfenyl chloride =  $\text{ClCH}_2\text{CH}_2\text{OS}(\text{O})\text{Cl}$ , h.p. 93–95° at 40 mm., 84–85° at 20 mm.,  $D_4^{20} = 1.5010$ , which upon attempted distn. at ord. press. dec. into  $\text{SO}_2 +$  ethylene (di)chloride (3:5130) (147). — However,  $\bar{\text{C}}$  (excess) with  $\text{SOCl}_2$  at elevated temp. (147) or  $\bar{\text{C}}$  (1 mole) with  $\text{SOCl}_2$  (1 mole) in cold (148) gives (75% yield (148)) cf. (156) *bis*-( $\beta$ -chloroethyl) sulfite =  $(\text{ClCH}_2\text{CH}_2\text{O})_2\text{SO}$ , b.p. 133° at 12 mm. (148), 117.5–118° at 4 mm. (147),  $D_4^{20} = 1.422$ ,  $n_D^{20} = 1.481$  (148).]

With sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ).  $\bar{\text{C}}$  with  $\text{SO}_2\text{Cl}_2$  in cold gives (149) (70% yield (122))  $\beta$ -chloroethyl chlorosulfonate =  $\text{ClCH}_2\text{CH}_2\text{O}\cdot\text{SO}_2\text{Cl}$  [Beil. I-2-(336)], b.p. 101° at 23 mm.,  $D_4^{20} = 1.552$ ,  $n_D^{20} = 1.4537$  (122). — However,  $\bar{\text{C}}$  with  $\text{SO}_2\text{Cl}_2$  under reflux (121) (or  $\beta$ -chloroethyl chlorosulfonate +  $\beta$ -chloroethyl nitrite (above) (122)) gives (50% yield (121)) *bis*-( $\beta$ -chloroethyl) sulfate =  $(\text{ClCH}_2\text{CH}_2\text{O})_2\text{SO}_2$  [Beil. I-2-(336)], b.p. 154–154.5° at 8 mm. (121), 130° at 3.5 mm. (122), m.p. + 11° (121),  $D_4^{20} = 1.4801$  (121),  $n_D^{20} = 1.4622$  (121), 1.4620 (122)].

With phosphoryl chloride ( $\text{POCl}_3$ ).  $\bar{\text{C}}$  with  $\text{POCl}_3$  at 0° (150) or in  $\text{CCl}_4$  at room temp. (151) gives (46–47% yield (151))  $\beta$ -chloroethylphosphoryl dichloride =  $\text{ClCH}_2\text{CH}_2\text{OP}(\text{O})\text{Cl}_2$  [Beil. I-2-(337)], b.p. 108–110° at 15 mm. (151). —  $\bar{\text{C}}$  with  $\text{POCl}_3$  in pyridine at –20° gives (140) the salt of mono-( $\beta$ -chloroethyl)phosphoric acid =  $\text{ClCH}_2\text{CH}_2\text{OP}(\text{O})(\text{OH})_2$  [Beil. I-1-(170), I-2-(336)]. —  $\bar{\text{C}}$  with  $\text{POCl}_3$  in  $\text{CCl}_4$  refluxed 16 hrs. gives (60% yield (152) cf. (140)) tri-( $\beta$ -chloroethyl) phosphate =  $(\text{ClCH}_2\text{CH}_2\text{O})_3\text{PO}$  [Beil. I-2-(337)], h.p. 180–182° at 2–3 mm.,  $D_4^{20} = 1.423$  (152). — For patent on reaction of  $\bar{\text{C}}$  with  $\text{POCl}_3$  see (153).]

With boron trifluoride ( $\text{BF}_3$ ).  $\bar{\text{C}}$  with  $\text{BF}_3$  forms a molecular compound (154)  $\text{BF}_3 \cdot 2\bar{\text{C}}$  which can be distilled in vac. without decompn.; b.p. 59° at 2 mm.,  $D_4^{20} = 1.4009$ ,  $n_D^{17} = 1.40841$  (154)].

With silicon tetrachloride ( $\text{SiCl}_4$ ).  $\bar{\text{C}}$  (4 moles) with  $\text{SiCl}_4$  (1 mole) yields (155) (96) tetra-( $\beta$ -chloroethyl) orthosilicate,  $(\text{ClCH}_2\text{CH}_2\text{O})_4\text{Si}$  [Beil. I-337, I-2-(337)], h.p. 195–200° at 15 mm. (156), 170–180° at 8 mm. (96) (also obtd. (156) from  $\text{SiCl}_4 + \beta$ -chloroethyl nitrite (above)).]

Behavior with alkalis.  $\bar{\text{C}}$  with alkalis (or appropriate acid acceptors) loses  $\text{HCl}$  to yield according to conditions either ethylene glycol (1:6465) or ethylene oxide (1:6105).

[E.g.,  $\bar{\text{C}}$  with aq.  $\text{NaOH}$  on htg. hydrolyzes to ethylene glycol (1:6465), for general articles on this process see (54) (157) (158) (22); for studies of kinetics of the reaction see (404) (18) (159) (160) (161); for examples of patents on hydrolysis of  $\bar{\text{C}}$  to ethylene glycol by use of aq. alkali or alkaline-earth hydronides, carbonates, or bicarbonates see (162) (163) (63) (164) (165) (166) (167).]

$\bar{\text{C}}$  added dropwise to 70% aq.  $\text{NaOH}$  (168) (169) or hot  $\text{CaO}$  (170) gives ethylene oxide (1:6105), h.p. +10.7°; for patents on this conversion see (171) (172) (173) (174) (175).]

Behavior with alkali sulfhydryte.  $\bar{\text{C}}$  with  $\text{NaSH}$  (from  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  satd. with  $\text{H}_2\text{S}$  (137)) at 55–65° (137) (176) or  $\bar{\text{C}}$  with  $\text{NaSH}$  in alc. for 36 hrs. at room temp. (177) gives (yields: 55% (176), 50–55% (137), 26–30% (177))  $\beta$ -hydroxyethyl mercaptan (“monothioethylene glycol”) =  $\text{HOCH}_2\text{CH}_2\text{SH}$  [Beil. I-470, I-2-(523)], h.p. 157–158° dec. at 742

mm. (178), 61° at 18 mm. (179), 58° at 18 mm. (137), 55° at 13 mm. (178), 52° at 12 mm. (177);  $D_4^{20} = 1.1143$  (178);  $n_D^{20} = 1.4996$  (178) (corresp. *bis*-(*N*-phenyl)carbamate, m.p. 146° (178); corresp. metallic mercaptide derivs. many of which have m.p.'s (178).]

**Behavior with ammonia** (for amines see below under behavior with organic reactants).  $\bar{C}$  with aq.  $NH_4OH$  gives (180) a mixt. of three hydroxyamines, viz.,  $\beta$ -hydroxyethylamine (2-aminoethanol-1) [Beil. IV-274, IV<sub>1</sub>-(424), IV<sub>2</sub>-(717)]; *bis*-( $\beta$ -hydroxyethyl)amine ("diethanolamine") [Beil. IV-283, IV<sub>2</sub>-(729)]; and *tris*-( $\beta$ -hydroxyethyl)amine ("triethanolamine") [Beil. IV-285, IV<sub>2</sub>-(729)]. — Although all three of these products are now extremely important industrial compounds, they are usually manufactured from ethylene oxide with  $NH_3$  and details lie beyond the scope of this text. — However, for a useful monograph see (181).]

**Behavior with hydrazine** ( $NH_2NH_2$ ).  $\bar{C}$  with 1 mole hydrazine loses HCl yielding (182)  $\beta$ -hydroxyethylhydrazine + hydrazine hydrochloride;  $\bar{C}$  with 2-3 moles hydrazine yields (182) ethylene oxide accompanied by a little *N,N*-*bis*-( $\beta$ -hydroxyethyl)hydrazine.]

#### BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

**Behavior with hydrocarbons.**  $\bar{C}$  with  $C_6H_6$  +  $AlCl_3$  (followed by aq.) is claimed (183) to yield  $\beta$ -phenylethyl alc. (1:6505), but this has subsequently been denied (184) where 1,2-diphenylethane (bibenzyl) (1:7149) and resin were the only prods. ohnd. (See also below under behavior of  $\bar{C}$  with organometallic cpds.)]

**Behavior with organic hydroxyl compounds.** With *alcohols* (see also below under carbohydrates).  $\bar{C}$  (anhydrous) with sodium alkoxides (from prim. or sec. aliphatic or arom. alcs. + Na) on htg. splits out NaCl giving the corresp. mono ethers of ethylene glycol.

[E.g.,  $\bar{C}$  with NaOMe gives (35% yield (185))  $\beta$ -hydroxyethyl methyl ether (1:6405) q.v.;  $\bar{C}$  with NaOEt gives (60% yield (185))  $\beta$ -hydroxyethyl ethyl ether (1:6410) q.v.;  $\bar{C}$  with NaOPr gives (40% yield (185))  $\beta$ -hydroxyethyl *n*-propyl ether (1:6414) q.v.;  $\bar{C}$  with NaOisPr gives (25% yield (185))  $\beta$ -hydroxyethyl isopropyl ether (1:6413) q.v.;  $\bar{C}$  with NaOBn gives (30% yield (185))  $\beta$ -hydroxyethyl *n*-butyl ether (1:6430) q.v.;  $\bar{C}$  with NaOis-Bu gives (36% yield (185))  $\beta$ -hydroxyethyl isohutyl ether (1:6235-A);  $\bar{C}$  with NaOAm gives (30% yield (185))  $\beta$ -hydroxyethyl *n*-amyl ether, b.p. 181° at 745 mm. (185).]  $\bar{C}$  with  $NaOCH_2C_6H_5$  similarly gives (186) (187) ethylene glycol monobenzyl ether (1:6533) q.v.]

With *carbohydrates* (or their relatives).  $\bar{C}$  with *d*-glucose + HCl yields (188) cf. (189) 2-chloroethyl-*d*-glucoside.]

$\bar{C}$  with "acetobromoglucose" +  $Ag_2CO_3$  (190) (193) in  $C_6H_6$  (189) (191) gives (yields: 69% (189), 45-50% (190)) tetra-acetyl- $\beta$ -*d*-( $\beta$ -chloroethyl)glucoside (tetra-acetyl- $\beta$ -*d*-glucosido-ethylene chlorohydrin), m.p. 119-120° (192), 118.5-119.5° (189), 114° cor. (190) (191). — For isomerization of this prod. (in boilg.  $CHCl_3$  for 6½ hrs.) to tetra-acetyl- $\alpha$ -*d*-( $\beta$ -chloroethyl)glucoside, m.p. 82-83°, see (194).]

$\bar{C}$  with "acetobromogalactose" +  $Ag_2CO_3$  (190) (194) in  $C_6H_6$  (191) gives (77% yield (194)) tetra-acetyl- $\beta$ -*d*-( $\beta$ -chloroethyl)galactoside, m.p. 117° cor. (190) (191), 115.5-116.5° (194).]

[For analogous prepn. from  $\bar{C}$  of triacetyl- $\beta$ -*d*-( $\beta$ -chloroethyl)xyloside, m.p. 137° cor., or of hepta-acetyl- $\beta$ -*d*-( $\beta$ -chloroethyl)lactoside, m.p. 78-80°, see (190) (191).]

[For condens. of  $\bar{C}$  with mannitol (1:5830) or sorbitol (1:5820) see (195).]

[For use of  $\bar{C}$  in degradation ("depolymerization") of cellulose or starch see (196) (197); for use of  $\bar{C}$  + NaOH in introduction of  $\beta$ -hydroxyethyl groups into cellulose see (198).]

With *aliphatic mercaptans*.  $\bar{C}$  with salts of alkyl or alkaryl mercaptans gives the corresp. S-monoethers of monothioethylene glycol.

[E.g.,  $\bar{C}$  with NaSMe in abs. alc. (199) (200) or ether (201) (202) or less advantageously

$\bar{C}$  with KSMc in aq. alc. (201) gives (yields 74–82% (199), 78% (201), 40% (199))  $\beta$ -hydroxyethyl methyl sulfide (*2-methylmercaptethanol*) [Beil. I-470 (524)], b.p. 80–85° at 30 mm. (201), 68–70° at 30 mm. (201), 68–70° at 30 mm. (201). —  $\bar{C}$  with MeI in dry ether.

iodide, hygroscop. cryst. from MeOH/ether, m.p. 60–62° (202). —  $\bar{C}$  with EtSH in alc./NaOEt (203), in alc. KOH (132), or even in conc. aq. KOH (204) gives (yield 70–74% (203))  $\beta$ -hydroxyethyl ethyl sulfide [Beil. I-470, I-7(525)], h.p. 184° (204) (132), 182–184° u.e. (203),  $D_4^{20} = 1.0166$  (132),  $n_D^{20} = 1.48669$  (132).]

[ $\bar{C}$  with *n*-BuSH in hot aq. NaOH refluxed 1 hr. gives (81% yield (205))  $\beta$ -hydroxyethyl *n*-butyl sulfide [Beil. I-7(525)], h.p. 92–93° at 3 mm.,  $D_4^{25} = 0.9693$ ,  $n_D^{20} = 1.4800$  (205). —  $\bar{C}$  with allyl mercaptan in conc. aq. KOH gives (50% yield (206))  $\beta$ -hydroxyethyl allyl sulfide [Beil. I-7(525)], h.p. 91° at 12 mm.,  $D_4^{20} = 1.0283$  (206). —  $\bar{C}$  with  $\text{NaSCH}_2\text{C}_6\text{H}_5$  in aq. soln. gives (100% yield (179))  $\beta$ -hydroxyethyl benzyl sulfide, b.p. 169° at 18 mm.]

[ $\bar{C}$  with ethylene dithioglycol ( $\text{HSC}_2\text{H}_4\text{CH}_2\text{SH}$ ) + powdered NaOH htd. 1 hr. gives (177) ethylene dithioglycol bis-( $\beta$ -hydroxyethyl ether) =  $\text{HOCH}_2\text{CH}_2\text{—S—CH}_2\text{CH}_2\text{—S—CH}_2\text{CH}_2\text{OH}$  [Beil. I-7(533)], lts., m.p. 62–63°.]

**With phenols.** [ $\bar{C}$  with phenol (1:1420) in aq. NaOH (207) or alc. NaOEt (208), or  $\bar{C}$  with  $\text{NaOC}_6\text{H}_5$  on htg. (17) (209), or  $\bar{C}$  with  $\text{KOC}_6\text{H}_5$  at 150° for 6 hrs. (210), or  $\bar{C}$  with phenol salt refluxed 8 hrs. (211) gives (yields: 84% (17), 79% (207), 55–62% (211), 50% (209))  $\beta$ -hydroxyethyl phenyl ether ( $\beta$ -phenoxyethanol) (1:6518) q.v., b.p. at 80 mm. = 165° (211), 163–166° (208), 163–167° (210), h.p. 128–130° at 20 mm. (17), 134–135° at 18 mm. (209). — (Note that  $\bar{C}$  with  $\text{NaOC}_6\text{H}_5$  in pres. of  $\text{Et}_3\text{N}$  gave only 12.5% yield (212) of  $\beta$ -phenoxyethanol.)]

[Similarly  $\bar{C}$  with aq. sodium *o*-nitrophenolate in s.t. at 125° for 20 hrs. gives (213)  $\beta$ -(*o*-nitrophenoxy)ethanol, oil, b.p. 180–182° at 4 mm., m.p. 35–36° (215) (corresp. acetate, oil; corresp. benzoate, m.p. 75–76° (213));  $\bar{C}$  with *m*-nitrophenol with 40% aq. KOH at 100° for 2 hrs. (213), or with 2 *N* NaOH refluxed 4 hrs. (214), gives  $\beta$ -(*m*-nitrophenoxy)ethanol, m.p. 90–91° (213), 88° (214), 87–88° (216);  $\bar{C}$  with sodium *p*-nitrophenolate in 50% alc. in s.t. at 120° for 23 hrs. (213), or in boilg. AmOH (216) (217), gives  $\beta$ -(*p*-nitrophenoxy)ethanol, m.p. 101–102° (213), 94–95° (216), 92–94° (215) (corresp. acetate, m.p. 85–87°, corresp. benzoate, m.p. 116° (213)).]

[Analogous condensations of  $\bar{C}$  with other monohydric phenols include the following: for  $\bar{C}$  with *o*-cresol (1:1400) (218), with  $\beta$ -naphthol (1:1540) (218), with *m*-methoxyphenol (1:1765) (219) (220) (221), with methyl *p*-hydroxybenzoate (1:1549) (222), with *p*-bromophenol (218), with *p*-acetylaminophenol (213), with *m*-diethylaminophenol (212), with 8-hydroxyquinoline (212) see indie. refs.]

[Analogous condensations of  $\bar{C}$  with polyhydric phenols include the following: with pyrocatechol (1:1520) (223), resorcinol (1:1530) (224) (218), 4-acetylresorcinol (219), 4-ethylresorcinol (219) see indie. refs.]

**With thiophenols.** [ $\bar{C}$  with thiophenol in alc. NaOEt (225) (203) or in 10% aq. KOH (226) gives (76% yield (203))  $\beta$ -hydroxyethyl phenyl sulfide, b.p. 245° (203), 144.5° at 26 mm. (203), 134–135° at 7 mm. (225), 115–116° at 2 mm. (226),  $D_4^{20} = 1.1431$  (226),  $n_D^{20} = 1.5897$  (225),  $n_D^{20} = 1.5917$  (226). —  $\bar{C}$  with *p*-tolyl mercaptan in conc. aq. NaOH at 100° for 2 hrs. gives (83% yield (133)) (227)  $\beta$ -hydroxyethyl *p*-tolyl sulfide, h.p. 282–283° dec., 174° at 30 mm. (133).]

[For analogous condens. of  $\bar{C}$  with *o*-nitrophenyl mercaptan (228), *m*-nitrophenyl mercaptan (228), *p*-nitrophenyl mercaptan (228) (229), *o*-carboxythiophenol (230), and many other thiophenols (231) see indie. refs.]

**Behavior of  $\bar{C}$  with organic ethers (or epoxy cpds.).** [ $\bar{C}$  with ethylene oxide (1:6105) + conc.  $\text{H}_2\text{SO}_4$  gives (30–35% yield (232)) 2-( $\beta$ -chloroethoxy)ethanol-1 (3:9185) accompanied



by other prods.: for behavior of  $\bar{C}$  with epichlorohydrin (3:5358) or with  $\alpha$ -ethyl- $\alpha$ -methyl-ethylene oxide see (232). —  $\bar{C}$  with  $\alpha,\beta$ -dichlorodiethyl ether (3:9150) stood 24 hrs. at room temp., then htd. 1 hr., gives (27% yield (233)) acetaldehyde bis-( $\beta$ -chloroethyl) acetal. (see below). —  $\bar{C}$  with bis-( $\alpha$ -chloroethyl) sulfide gives (234)  $\beta$ -trithioacetaldehyde, m.p. 125°. — For behavior of  $\bar{C}$  with 2,3-dichlorodioxane (3:9105) see (235); with 1,4-dithiane see (131).]

Behavior of  $\bar{C}$  with carbonyl compounds.  $\bar{C}$  with aldehydes or their polymers. [ $\bar{C}$  with paraformaldehyde (1:0080) + dry HCl gas gives (yields: 65% (237), 55% (236)) (238) (239) chloromethyl  $\beta$ -chloroethyl ether [Beil. I-581, I<sub>2</sub>-(645)], b.p. 145-147° (237), 46° at 10 mm. (236);  $D_4^{20} = 1.2817$  (237), 1.2814 (236);  $n_D^{20} = 1.4578$  (236), 1.4592 (237). — Note that this prod. with  $\bar{C}$  (239), or  $\bar{C}$  (8 wt. pts.) + paraformaldehyde (1 wt. pt.) +  $\text{CaCl}_2$  + HCl gas refluxed 5 min. (35) gives formaldehyde bis-( $\beta$ -chloroethyl)acetal [Beil. I-575], b.p. 218-219° (239), 218.1° at 760 mm. (240), b.p. 93-94° at 11 mm. (38), now an industrial prod. in U.S. because of its use in manufact. of self-sealing gasoline tanks (240).]

[ $\bar{C}$  with acetaldehyde (1:0100) (241) (233) or paraldehyde (1:0170) (236) + HCl gas gives according to circumstances either  $\alpha$ -chloroethyl  $\beta$ -chloroethyl ether (3:9150) q.v. or acetaldehyde bis-( $\beta$ -chloroethyl)acetal, b.p. 194-196° dec. (233), 109-110° at 30 mm. (20), 106° at 17 mm.,  $D_4^{19} = 1.1712$ ,  $n_D^{16.2} = 1.4532$  (233).]

[ $\bar{C}$  with propionaldehyde (1:0110) + HCl gas gives (51% yield (236))  $\beta$ -chloroethyl  $\alpha$ -chloro-*n*-propyl ether, b.p. 60° at 10 mm.,  $D_4^{20} = 1.1399$ ,  $n_D^{20} = 1.4496$  (236).]

[ $\bar{C}$  with *n*-butyraldehyde (1:0130) + HCl gas gives (70% yield (236))  $\beta$ -chloroethyl  $\alpha$ -chloro-*n*-butyl ether, b.p. 71° at 10 mm.,  $D_4^{20} = 1.1009$ ,  $n_D^{20} = 1.4471$  (236).]

$\bar{C}$  with diketene. [ $\bar{C}$  with diketene (242) gives (243)  $\beta$ -chloroethyl acetoacetate.]

Behavior of  $\bar{C}$  with organic acids.  $\bar{C}$  with organic acids under appropriate conditions behaves conventionally as a substituted ethyl alcohol yielding the corresponding  $\beta$ -chloroethyl esters. Since the number of possibilities is enormous, no attempt can be made here to list all such cases; only a few typical examples must suffice. Note, moreover, that, because during ordinary esterification hydrolysis of the chlorine atom of  $\bar{C}$  may occur, many esters of  $\bar{C}$  are best made from its reaction with acyl halides q.v.

[ $\bar{C}$  with anhydrous formic acid (1:1003) in pres. of anhydr.  $\text{Na}_2\text{SO}_4$  (244) or of HCl gas (245) gives  $\beta$ -chloroethyl formate, b.p. 132° at 764 mm. (245), 127-129° at 768 mm. (244),  $D_4^{20} = 1.2214$  (244); for study of rate of esterification of  $\bar{C}$  by formic acid under various circumstances see (246).]

[ $\bar{C}$  with anhydr. oxalic acid (1:0535 on satn. with HCl gas and htd. at 100° gives (245) di-( $\beta$ -chloroethyl) oxalate (3:0572), m.p. 45°.]

[ $\bar{C}$  with 2-hydroxy-5-methylbenzoic acid (*p*-cresotinic acid) + conc.  $\text{H}_2\text{SO}_4$  gives  $\beta$ -chloroethyl *p*-cresotinate, b.p. 136-139° at 10 mm. (247).]

[ $\bar{C}$  with *p*-aminobenzoic acid + conc.  $\text{H}_2\text{SO}_4$  gives (248) (249)  $\beta$ -chloroethyl *p*-aminobenzoate.]

Behavior of  $\bar{C}$  with salts of organic acids.  $\bar{C}$  with sodium salts of organic acids on htd. eliminates NaCl yielding the corresp.  $\beta$ -hydroxyethyl esters; however, not infrequently secondary reactions of this product then occur or can readily be caused to occur, such as loss of water, ring closure, etc.

[ $\bar{C}$  with aq. NaCN at 45-50° for 5 hrs. (250) (251), or with alc. NaCN at 100° for 6 hrs. (58) (27), or with KCN in 50% alc. (252) or boilg. alc. (253) (254), gives (yields: 86% (27), 85-95% (251), 79-80% (250), 71% (253))  $\beta$ -hydroxyethyl cyanide ( $\beta$ -hydroxypropionitrile = hydracrylonitrile = ethylene cyanohydrin) [Beil. III-298, III<sub>1</sub>-(113), III<sub>2</sub>-(213)], b.p. 116-118° at 20 mm. (250), 110° at 15 mm. (27) (253), 107-109° at 12 mm. (250).]

[ $\bar{C}$  (1 mole) with  $\text{NaHCO}_3$  (1 mole solid) or with  $\text{Na}_2\text{CO}_3$  ( $\frac{1}{2}$  mole solid) as directed (255) is claimed to give (80% yield) monomeric ethylene glycol carbonate  $(\text{CH}_2)_2\text{O}_2\text{CO}$ .]

[ $\bar{C}$  (1 mole) with KSCN (1 mole) in excess  $\bar{C}$  (1.5 moles as solv.) on warming does not yield the expected  $\beta$ -hydroxyethyl thiocyanate, since this prod. spontaneously undergoes bimolecular self-condensation evolving COS and producing (45% yield (256)) 1-( $\beta$ -hydroxyethyl)imidazolidithione-2, m.p. 167–168° dec.; for behavior of this prod. with ethereal HCl see (257).]

[ $\bar{C}$  with NaOBz at 145° (258) or  $\bar{C}$  with NaOBz + a little  $Et_2NH$  at 130° for 4 hrs. (259), or  $\bar{C}$  with KOBz as directed (260), gives (yields: 85% (259), 33% (260)) ethylene glycol monobenzoate ( $\beta$ -hydroxyethyl benzoate), m.p. 36.5–37.5° (261), 36–37° (260) cf. (259); b.p. 173° at 21 mm. (259), 156° at 14 mm. (260), 150–151° at 10 mm. (261) (corresp. p-toluenesulfonate, m.p. 74–75° (262)).]

[ $\bar{C}$  with Na p-nitrobenzoate + a little  $Et_2NH$  at 130° for 4 hrs. (259), or  $\bar{C}$  with K p-nitrobenzoate in  $C_6H_6$  in s.t. at 100° (263), gives (yields: 83% (259), 60% (263)) ethylene

indic. refs.]

Behavior of  $\bar{C}$  with acid chlorides of organic acids.  $\bar{C}$  with acid chlorides of organic acids behaves as a substituted primary alcohol splitting out H from its OH with Cl from the acid chloride to yield the corresp.  $\beta$ -chloroethyl esters. No attempt can be made here to list all possible cases, but the following text will furnish ample illustrative examples.

With acid chlorides of aliphatic acids. [ $\bar{C}$  with acetyl chloride (3:7085) gives (yields: 90% (267), 82% (248)) (268)  $\beta$ -chloroethyl acetate (3:5735) q.v. —  $\bar{C}$  with trichloroacetyl chloride (3:5420) + pyridine in ether gives (45% yield (103)) (275)  $\beta$ -chloroethyl trichloroacetate (3:6510) q.v. —  $\bar{C}$  with sorbly chloride ( $CH_2CH=CH-CH=CH-CO.Cl$ ) [Beil. I-484, I-(453)] gives alm. quant (269)  $\beta$ -chloroethyl sorbate, b.p. 115° at 15 mm. (269). — For studies of rate of reactn. of  $\bar{C}$  with various acyl chlorides in dioxane soln. at 15°, 25°, and 35° see (270). —  $\bar{C}$  with malonyl (di)chloride (3:9030) gives bis-( $\beta$ -chloroethyl) malonate, b.p. 164° at 15 mm. (271).]

With various chloroformates.  $\bar{C}$  with carbonyl chloride (phosgene) (3:5000) at room temp. gives (61% yield (274))  $\beta$ -chloroethyl chloroformate (3:5780) q.v. [ $\beta$ -chloroethyl chloroformate (3:5780) below] is formed.]

(274)  $\beta$ -chloroethyl trichloromethyl carbonate =  $ClCH_2CH_2O.CO.O.CCl_3$ , h.p. 115° at 16 mm., 110° at 12 mm.,  $D_4^{20} = 1.5664$ ,  $n_D^{20} = 1.4748$  (274).]

[ $\bar{C}$  with  $\beta$ -chloroethyl chloroformate (3:5780) gives (70% yield (121)) di-( $\beta$ -chloroethyl) carbonate (3:6790) q.v.]

With acid chlorides of aromatic acids. [ $\bar{C}$  with benzoyl chloride on htg. gives (yields: 90% (276), 84.5% (277), 55% (263))  $\beta$ -chloroethyl benzoate (3:8860) q.v.]

Behavior of  $\bar{C}$  with organic esters of inorganic acids. [ $\bar{C}$  with  $Me_2SO_4$  at 120° as directed gives (60% yield (126))  $\beta$ -chloroethyl methyl ether ( $\beta$ -methoxyethyl chloride) (3:7265) q.v.]

[ $\bar{C}$  with  $Et_2SO_4$  + solid NaOH on htg. gives (278) ethylene glycol monoethyl ether ("Cellosolve") (1:6410); note, however, that  $\bar{C}$  with  $EtOH$  + conc.  $H_2SO_4$  at 145° gives (279)  $\beta$ -chloroethyl ethyl ether (3:7463).]

[ $\bar{C}$  (1 mole) with ethyl metaphosphate (1 mole) stood 4 days at room temp. (280) cf. (281) gives  $\beta$ -chloroethyl ethyl hydrogen phosphate (isolated as harium salt); however,  $\bar{C}$  + ethyl metaphosphate in  $CHCl_3$  refluxed 3 hrs. gives (140)  $\beta$ -chloroethyl dihydrogen phosphate (isolated as harium salt).]

$\bar{C}$  with organic hypochlorites (or mixtures which yield them) gives ethers [e.g.,  $\bar{C}$  with *tert*-butyl hypochlorite (3:7165) + ethylene gives (60.8% yield (282))  $\beta, \beta'$ -dichlorodiethyl

ether (3:6025). —  $\bar{C}$  with *N,N*-dichlorobenzenesulfonamide + butene-1 in  $\text{CHCl}_3$  at  $-15^\circ$  gives (283) (probably via formn. and addn. of  $\beta$ -chloroethyl hypochlorite) 1-chloro-2-( $\beta$ -chloroethoxy)butane, b.p.  $195.5^\circ$ ,  $D_4^{20} = 1.1223$ ,  $n_D^{20} = 1.453$ ; the use of butene-2 or of 2-methylpropene (isobutylene) gives analogous products (283) cf. (284).]

Behavior of  $\bar{C}$  with organometallic compounds (or their equivalents). [ $\bar{C}$  with  $\text{KC}_6\text{H}_5$  splits out  $\text{KCl}$  yielding (285)  $\beta$ -phenylethyl alc. (1:6505).]

$\bar{C}$  with arom.  $\text{RMgX}$  cpds. reacts in analogous fashion yielding the corresp. alcohols [e.g.,  $\bar{C}$  with  $\text{C}_6\text{H}_5\text{MgBr}$  (287) (288) or  $\text{C}_6\text{H}_5\text{MgCl}$  (289) gives (95% yield (286))  $\beta$ -phenylethyl alc. (1:6505);  $\bar{C}$  with *o*-tolyl  $\text{MgBr}$  gives (20–24% yield (290)) (287)  $\beta$ -(*o*-tolyl)-ethanol;  $\bar{C}$  with *m*-tolyl  $\text{MgBr}$  gives (20–24% yield (290))  $\beta$ -(*m*-tolyl)ethanol;  $\bar{C}$  with *p*-tolyl  $\text{MgBr}$  gives (yields: 80% (291), 20–24% (290)) (287)  $\beta$ -(*p*-tolyl) ethanol; many other analogous cases are known].

[Note that  $\bar{C}$  with  $\text{C}_2\text{H}_5\text{MgBr}$  gives (292)  $\text{ClCH}_2\text{CH}_2\text{OMgBr}$  which may then be reacted with  $\text{RMgBr}$  types as above (292).]

[ $\bar{C}$  with diethyl malonate in alc.  $\text{NaOEt}$  (i.e., diethyl disodiomalonnate) might be expected to yield diethyl *bis*-( $\beta$ -hydroxyethyl)malonnate; this compd., however, is unknown since it loses 2  $\text{EtOH}$ , ring-closing to (271) the spiro-dilactone of *bis*-( $\beta$ -hydroxyethyl)malonic acid [Beil. XIX<sub>1</sub>-(680)], m.p.  $109\text{--}110^\circ$ .] — [Note also that  $\bar{C}$  (1 mole) with diethyl malonate (1 mole) + 1%  $\text{HCl}$  gas undergoes transesterification yielding (405) both  $\beta$ -chloroethyl ethyl malonate, b.p.  $105\text{--}106^\circ$  at 3 mm., and *bis*-( $\beta$ -chloroethyl) malonate, b.p.  $142\text{--}143^\circ$  at 3 mm.]

[ $\bar{C}$  with ethyl acetoacetate + alc.  $\text{NaOEt}$  (i.e., ethyl sodio-acetoacetate) boiled 5 hrs. gives a prod. (probably lactone of  $\alpha$ -( $\beta$ -hydroxyethyl)acetoacetic acid) which with 10%  $\text{HCl}$  after 5 hrs. boiling gives (40% yield (293)) pentanone-4-ol-1 ( $\gamma$ -aceto-*n*-propyl alc.) [Beil. I-831, I<sub>1</sub>-(422), I<sub>2</sub>-(873)], b.p.  $115\text{--}116^\circ$  at 20 mm. (204),  $D_4^{20} = 1.0071$  (205),  $n_D^{20} = 1.439$  (294) (corresp. semicarbazone, m.p.  $167\text{--}168^\circ$  (296)): note that this prod. (which is an important intermediate in the prepn. of the antimalarial "Atabrine" (297)) is best prepd. from ethylene oxide + ethyl sodioacetoacetate which gives first (60% yield (294)) the lactone of  $\alpha$ -( $\beta$ -hydroxyethyl)acetoacetic acid, b.p.  $142\text{--}143^\circ$  at 30 mm.,  $n_D^{20} = 1.4562$ , which with warm  $\text{HCl}$  ring-opens and splits off  $\text{AcOH}$  giving (66% yield (294)) desired  $\gamma$ -aceto-*n*-propyl alc. (above).]

[ $\bar{C}$  + sodium phenobarbital (Na deriv. of 5-ethyl-5-phenylbarbituric acid) gives (60% yield (298)) 1-( $\beta$ -hydroxyethyl)phenobarbital, m.p.  $145.0\text{--}145.5^\circ$  cor. (note that this prod. is *not* obtd. from  $\bar{C}$  + Ag salt of phenobarbital). —  $\bar{C}$  with theobromine (3,7-dimethylxanthine) in aq.  $\text{NaOH}$  in s.t. at  $125^\circ$  for 6 hrs. gives (47–57% yield (366)) (367) 1-( $\beta$ -hydroxyethyl)theobromine, m.p.  $194^\circ$  (367),  $193^\circ$  (366).]

Behavior of  $\bar{C}$  with amines. With primary aliphatic amines. [ $\bar{C}$  (1 mole) with aq.  $\text{MeNH}_2$  (1 mole) at  $110^\circ$  for 12–24 hrs gives (80% yield (299))  $\beta$ -(methylamino)ethanol [Beil. IV-276, IV<sub>2</sub>-(718)], h.p.  $159^\circ$  (300) (301),  $155\text{--}156^\circ$  at 760 mm. (273) (corresp. 3,5-dinitrobenzoate, m.p.  $195\text{--}196.5^\circ$  (302); corresp.  $\text{B.PkOH}$ ,  $148^\circ$  (303); corresp. reaction prod. with  $\alpha$ -naphthyl isothiocyanate, viz., *N*-( $\beta$ -hydroxyethyl)-*N*-methyl-*N'*-( $\alpha$ -naphthyl) thiourea, m.p.  $125^\circ$  (303)). —  $\bar{C}$  with excess aq.  $\text{MeNH}_2$  on standing in s.t. at  $100^\circ$  for several hrs. (304) or  $\bar{C}$  with  $\beta$ -(methylamino)ethanol (above) in aq. at  $120^\circ$  (299) gives methyl-*bis*-( $\beta$ -hydroxyethyl)amine (*N*-methyl-diethanolamine) [Beil. IV-284, IV<sub>2</sub>-(729)], b.p.  $115^\circ$  at 5 mm. (240) (note that this prod. is new commercial chem. in U.S. (240)).]

[ $\bar{C}$  with  $\text{EtNH}_2$  as above should give  $\beta$ -(ethylamino)ethanol [Beil. IV-282, IV<sub>2</sub>-(727)], b.p.  $167\text{--}169^\circ$  cor. at 751 mm.,  $D_4^{20} = 0.914$ ,  $n_D^{20} = 1.444$ , and (305) ethyl-*bis*-( $\beta$ -hydroxyethyl)amine (*N*-ethyl-diethanolamine) [Beil. IV-284], although both these prods. are usually prepd. from ethylene oxide.]

[For analogous reactn. of  $\bar{C}$  with *n*-heptadecylamine yielding *N*-( $\beta$ -hydroxyethyl)-*n*-

heptadecylamine see (306) (307); with cyclohexylamine yielding *N*-( $\beta$ -hydroxyethyl)-cyclohexylamine see (308).]

With primary aromatic amines  $\bar{C}$  (1 mole) with aniline (1 mole) refluxed a short time (299) (309) (310) (311) (312) (313) gives (yields: 70% (309), 40% (311)) *N*-( $\beta$ -hydroxyethyl)aniline ( $\beta$ -phenylaminoethanol) [Beil. XII-182], b.p. 286° cor. (299),  $n_D^{20} = 1.5740$  (317) (note that by reactn. of a second mole of  $\bar{C}$  some *N,N*-bis-( $\beta$ -hydroxyethyl)aniline (see below) may also form, and that some *N,N'*-diphenylethylenediamine, m.p. 63.4–64.2°, may also appear (311)), note also that *N*-( $\beta$ -hydroxyethyl)aniline on dehydration, e.g. by htg. in xylene with  $P_2O_5$  (310), reacts bimolecularly giving in small yield *N,N'*-diphenylpiperazine, m.p. 160–162° (310) —  $\bar{C}$  (2 moles) with aniline (1 mole) especially in pres. of anhydr.  $Na_2CO_3$  (310) or NaOH (314) or aq. at 110° (299) gives *N,N*-bis-( $\beta$ -hydroxyethyl)aniline (*N*-phenyldiethanolamine) [Beil. XII-183, XII-(167)], m.p. 58° (315), 53.5–54° (310); note that this prod. on htg. at 200° under reduced press. (314) or htg. with  $P_2O_5$  in xylene (310) or htg. with 70%  $H_2SO_4$  at 160° (316) loses water and ring-closes to *N*-phenylmorpholine [Beil. XXVII-6], m.p. 53° (299), 52° (310).]

$\bar{C}$  (1 mole) with *o*-toluidine (2 moles) at 120–130° for several hrs. (318) (313) gives  $\beta$ -(*o*-tolylamino)ethanol, b.p. 172° at 12 mm. (318), 145–150° at 3 mm. (317),  $n_D^{20} = 1.5675$  (317); note that in pres. of  $Na_2CO_3$  the main (318) prod. (because of bimolecular condens. of this prod.) is *N,N'*-di-*o*-tolylpiperazine [Beil. XXIII-8], m.p. 174°. —  $\bar{C}$  with *p*-toluidine on htg. gives (319)  $\beta$ -(*p*-tolylamino)ethanol [Beil. XII-907], b.p. 177–178° at 14 mm. (319), m.p. 42–43° (317); note, however, that analogous bimolecular ring closure of this prod. readily occurs on htg. yielding (320) *N,N'*-di(*p*-tolyl)piperazine [Beil. XX(II)-9], m.p. 190°.]

$\bar{C}$  with *o*-methoxyaniline (*o*-anisidine) at 100° for 48 hrs. gives (75–80% yield (321)) (299)  $\beta$ -(*o*-methoxyphenylamino)ethanol [Beil. XIII-367], b.p. 303° cor. (299) (corresp.  $HCl$ , m.p. 131°;  $H.PkOH$ , m.p. 140° (321)), note that this prod. with 5 pts. conc.  $HCl$  in *s.t.* at 160–180° gives by a remarkable elimination of  $MeOH$  and monomolecular ring closure (38% yield (321)) (299) "phenmorpholine" [Beil. XXVII-31], b.p. 268° cor. (299), 127–128° at 12 mm. (321). —  $\bar{C}$  with *p*-ethoxyaniline (*p*-phenetidine) gives on htg. (319)  $\beta$ -(*p*-ethoxyphenylamino)ethanol, m.p. 67°, b.p. 190° at 11 mm. (319) cf. (322).]

Many other cases, analogous to the above examples, are also known but cannot be included here.

With secondary aliphatic amines. Because of the great importance of  $\beta$ -(dialkylamino)-ethanols in the prepn. and study of physiologically active compounds, much study has been given to their prepn. from  $\bar{C}$  (and otherwise). From the resulting mass of data, the following examples are cited.

$\bar{C}$  with  $Me_2NH$  gives (323)  $\beta$ -(dimethylamino)ethanol [Beil. IV-276, IV-(425), IV-(719)], b.p. 135° cor. at 758 mm.,  $D_4^{20} = 0.8556$ ,  $n_D^{20} = 1.4300$  (324) (corresp. *p*-nitrobenzoyl ester, m.p. 55° (325)). —  $\bar{C}$  with  $Et_2NH$  on htg. (326) under reflux for 8 hrs. (327) or in pres. of NaOH under press. at 160° for 3 hrs. (328) gives (yields: 83% (328), 68–70% (327))  $\beta$ -(diethylamino)ethanol [Beil. IV-282, IV-(727)], b.p. 163° at 760 mm. (329), 160° at 741 mm., 160° at 80 mm., 96° at 73 mm., 53° at 10 mm. (330), 42–44° at 8 mm. (329);  $D_4^{20} = 0.8501$  (329);  $n_D^{20} = 1.4409$  (329), 1.4389 (330) (corresp. *N*-(*p*-nitrophenyl)carbamate, m.p. 59–60° cor. (329)).]

$\bar{C}$  with di-*n*-propylamine under reflux gives (70% yield (331))  $\beta$ -(di-*n*-propylamino)-ethanol [Beil. IV-282], b.p. 99–92° at 22 mm. (331) (corresp. *p*-nitrobenzoyl ester hydrochloride, m.p. 133.5–134.5° (325)). —  $\bar{C}$  with di-*n*-butylamine on htg. gives (332) (333)  $\beta$ -(di-*n*-butylamino)ethanol, b.p. 225–230° at 760 mm., *sl. dec.* (332), 226–228° at 738 mm. (332), 90–91° at 7 mm. (333);  $D_4^{20} = 0.8624$  (325);  $n_D^{20} = 1.4444$  (325) (corresp. *p*-nitrobenzoyl ester hydrochloride, m.p. 92.5–93.5° (325) (332)). —  $\bar{C}$  with di-(*sec*-butyl)amine

isocyanate but always by indirect means; note also that on short boilg. with aq. or alc. alk. it loses HCl and by ring closure yields 3-phenyloxazolidone [Beil. XXVII-136], lfts. from alc., m.p. 124° (272), 122° (309).]

⑥  $\beta$ -Chloroethyl *N*-(*p*-bromophenyl)carbamate: pl. from lgr.; m.p. 88–89° (400). [From  $\bar{C}$  with *p*-bromobenzazide (400).]

⑦  $\beta$ -Chloroethyl *N*-( $\alpha$ -naphthyl)carbamate [Beil. XII-1236]: m.p. 102–103° (373), 101° (391) (93), 100–101° (309). [From  $\bar{C}$  with  $\alpha$ -naphthyl isocyanate (391) (373); also from  $\beta$ -chloroethyl chloroformate (3:5780) with  $\alpha$ -naphthylamine (309): note also that with dil. KOH (309) this prod. loses HCl ring-closing to 3-( $\alpha$ -naphthyl)-oxazolidone-2 [Beil. XXVII-136], m.p. 125° (309), while with conc. KOH it merely undergoes hydrolysis of chlorine yielding *N*-( $\beta$ -hydroxyethyl)- $\alpha$ -naphthylamine, m.p. 52° (309).]

—  $\beta$ -Chloroethyl *N*-( $\beta$ -naphthyl)carbamate [Beil. XII-1292]: m.p. 98° (309). [Prepd. indirectly from  $\beta$ -chloroethyl chloroformate (3:5780) with  $\beta$ -naphthylamine (309); for behavior with dil. and conc. KOH analogous to preceding case see (309).]

⑧  $\beta$ -Chloroethyl *N*-carbamidocarbamate ( $\beta$ -chloroethyl allophanate) [Beil. III<sub>2</sub>-(56)]: m.p. 182.5° (392), 181–182° (388). [From  $\bar{C}$  with vapors of isocyanic acid (392) or from  $\beta$ -chloroethyl chloroformate (3:5780) with urea (388).]

— *N*-( $\beta$ -hydroxyethyl)phthalimide = ( $\beta$ -(*N*-phthalimido)ethanol) [Beil. XXI-469, XXI<sub>1</sub>-(368)]: m.p. 129.5° cor. (394), 127–128° (395), 126.5–127.6° (357), 126–127° (396), 125–120° (397) (note that m.p. given by (393) is incorrect). [From  $\bar{C}$  with K phthalimide in a.t. at 150° for 4 hrs. (393): note that the m.p. of 88–89° reported by the only worker (393) using this method is not far from that (81° (395)) of *N*-( $\beta$ -chloroethyl)phthalimide leaving some question as to which prod. was really obt'd.].

⑨ *N*-( $\beta$ -hydroxyethyl)tetrachlorophthalimide: m.p. 208–209° (398). [From  $\bar{C}$  with K tetrachlorophthalimide in a.t. at 200° for 6 hrs. (398).]

—  $\beta$ -Chloroethyl triphenylmethyl ether: m.p. 132° (399). [From  $\bar{C}$  with  $\alpha$ -bromo-triphenylmethane (399).]

3:5552 (1) — 1952 1953 1954 1955 1956 1957 1958 1959 1960 1961 1962 1963 1964 1965 1966 1967 1968 1969 1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1981 1982 1983 1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023 2024 2025 2026 2027 2028 2029 2030 2031 2032 2033 2034 2035 2036 2037 2038 2039 2040 2041 2042 2043 2044 2045 2046 2047 2048 2049 2050 2051 2052 2053 2054 2055 2056 2057 2058 2059 2060 2061 2062 2063 2064 2065 2066 2067 2068 2069 2070 2071 2072 2073 2074 2075 2076 2077 2078 2079 2080 2081 2082 2083 2084 2085 2086 2087 2088 2089 2090 2091 2092 2093 2094 2095 2096 2097 2098 2099 2100 2101 2102 2103 2104 2105 2106 2107 2108 2109 2110 2111 2112 2113 2114 2115 2116 2117 2118 2119 2120 2121 2122 2123 2124 2125 2126 2127 2128 2129 2130 2131 2132 2133 2134 2135 2136 2137 2138 2139 2140 2141 2142 2143 2144 2145 2146 2147 2148 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(51) Moureu, Dodé, *Bull. soc. chim.* (5) 4, 281-295 (1937); *Compt. rend.* 203, 802-804 (1936). (52) Frahm, *Rec. trav. chim.* 50, 261-267 (1931). (53) Bozza, Mamoli, *Giorn. chim. ind. applicata* 12, 283-292 (1930), *Cent.* 1939, II 1854, *C.A.* 24, 5021 (1930). (54) Brooks, *Chem. Met. Eng.* 22, 629-633 (1920). (55) Shulov, Kanyayev, Domina, Ionina, *J. Phys. Chem. (U.S.S.R.)* 13, 1242-1248 (1939), *C.A.* 33, 371 (1941). (56) Zimakov, Gripiich, *Org. Chem. Ind. (U.S.S.R.)* 1, 396-404 (1936), *Cent.* 1937, I 1012; *C.A.* 30, 6705 (1936). (57) Tropsch, Kessler, *Mitt. Kohlenforsch. Inst. Prag* 1931, No. 1, 16-42, *Cent.* 1932, I 2159, *C.A.* 26, 1242 (1932). (58) Zapadnaskii, *J. Chem. Ind. (Moscow)* 5, 1426-1429 (1928); *C.A.* 23, 3208 (1929), not in *Cent.* (59) Shulov, *J. Chem. Ind. (Moscow)* 5, 1273-1276 (1928); *Cent.* 1929, II 1646; *C.A.* 23, 2937 (1929). (60) Carlius, *Ann.* 126, 195-199 (1865), *Butlerov, Ann.* 144, 40-42 (1867).

(61) Britton, Nutting, Hüscher (to Dow Chem. Co.), U.S. 2,130,226, Sept. 13, 1938; *Cent.* 1939, I 1856, *C.A.* 32, 9096 (1938). (62) Youtz (to Standard Oil Co.), U.S. 1,875,309, Aug. 30, 1932; *Cent.* 1933, II 2053, *C.A.* 26, 5971 (1932). (63) Essex, Ward (to du Pont Co.), U.S. 1,826,398, April 26, 1927; *Cent.* 1928, I 410; *C.A.* 21, 2136 (1927). (64) Essex, Ward (to du Pont Co.), U.S. 1,594,608, Aug. 3, 1926; *Cent.* 1926, II 1693, *C.A.* 20, 3170 (1926). (65) McElroy, U.S. 1,510,790, Oct. 7, 1924, *C.A.* 19, 77 (1925), not in *Cent.* (66) Brooks, 1,498,781, 1,498,782, June 24, 1924; *Cent.* 1924, II 1631, *C.A.* 18, 2606 (1924). (67) Irvine, Haworth (to Carbide and Carbon Chem. Corp.), U.S. 1,496,675, June 3, 1924; *Cent.* 1924, II 1510; *C.A.* 18, 2345 (1924). (68) Young, U.S. 1,456,959, May 29, 1923; *C.A.* 17, 2428 (1923); not in *Cent.* (69) Curme, Young, U.S. 1,456,916, May 29, 1923; *C.A.* 17, 2428, not in *Cent.* (70) Eldred, U.S. 1,456,590, May 29, 1923, *C.A.* 17, 2428, not in *Cent.*

(71) Brooks (to Chateloid Chem. Co.), U.S. 1,394,664, Oct. 25, 1921; *Cent.* 1922, IV 941; *C.A.* 16, 423 (1922). (72) Finkelstein (to I.G.), *Canadian* 285,920, Dec. 25, 1928, *Cent.* 1932, I 1153; *C.A.* 23, 1138 (1929). (73) Curme, Young, *Canadian* 238,729, March 18, 1924; *Cent.* 1925, I 1129, not in *C.A.* (74) Kennedy, Barker (to Shawinigan Chem. Ltd.), *Brit.* 552,319, April 1, 1943; *C.A.* 38, 3992 (1944). (75) Soc. Carbochem., *Brit.* 445,011, April 30, 1936; *Cent.* 1936, II 1244, [*C.A.* 39, 6390 (1936)]. *French* 795,804, March 23, 1936; *C.A.* 39, 5592 (1936); not in *Cent.* (76) Tropsch, Kessler, *Brit.* 377,595, Aug. 18, 1932, *Cent.* 1932, II 2724, [*C.A.* 27, 3944 (1933)]. *French* 732,106, Feb. 17, 1932, *C.A.* 27, 732 (1933), not in *Cent.* (77) Long, Willson, Wheeler, *Brit.* 265,269, March 3, 1927; *Cent.* 1927, II 2350; *C.A.* 22, 244 (1928). (78) Marks (to Carbide and Carbon Chem. Corp.), *Brit.* 235,044, July 2, 1925; *Cent.* 1928, II 711; *C.A.* 20, 917 (1926). *Ger.* 527,940, June 24, 1931; *Cent.* 1931, II 1753; [*C.A.* 25, 5177 (1931)]. (79) T. Goldschmidt, A.G., *Ger.* 538,915, July 12, 1927, *C.A.* 26, 2198 (1932); not in *Cent.*; *Belgian* 352,582, Jan. 8, 1929, *Cent.* 1931, I 2932; not in *C.A.*; *French* 656,947, May 15, 1929; *Cent.* 1929, II 648; [*C.A.* 23, 4231 (1929)]. *Brit.* 293,754, July 11, 1927; *C.A.* 23, 1651 (1929); not in *Cent.* (80) Union Chem. Belg., *French* 829,493, June 28, 1938, *Cent.* 1938, II 3316; *C.A.* 33, 993 (1939). (81) Comp. Prod. Chim. d'Alais, etc., *French* 785,170, Aug. 3, 1935; *Cent.* 1936, I 1309; *C.A.* 30, 492 (1936). (82) Dammens, de Loisy, Piette, *French* 535,210, April 11, 1922, *Cent.* 1923, II 741, not in *C.A.* (83) Iskra, *J. Chem. Ind. (Moscow)* 12, 947-953 (1935); *Cent.* 1936, I 2823; *C.A.* 30, 711 (1936). (84) Harford (to A. D. Little, Inc.), U.S. 2,107,789, Feb. 8, 1938; *Cent.*

{361} Meerwein, Hinz, *Ann.* 484, 17, 22-23 (1930). {362} Fromm, Honold, *Ber.* 55, 006-009 (1922). {363} Fromm, *Ann.* 442, 139-140 (1925). {364} Ercoli, *Ann. chim. applicata* 25, 263-273 (1935); *Cent.* 1935, II 3090; *C.A.* 30, 1028 (1936). {365} Yang, Johnson, *J. Am. Chem. Soc.* 54, 2971 (1932). {366} Rojahn, Fegeler, *Arch. Pharm.* 268, 568-569 (1930). {367} Béhal (to

Austrian 101,671, Nov. 25, 1925; *Cent.* 1926, II 1585; not in *C.A.* {373} Jones, Burns, *J. Am. Chem. Soc.* 47, 2973 (1925). {374} Blicke, Castro, *J. Am. Chem. Soc.* 63, 2438 (1941). {375} Földi, *Ber.* 53, 1837 (1920). {376} von Kereszty, Wolf, *Ger.* 353,195, May 12, 1922; *Cent.* 1922, IV 156; *C.A.* 17, 1243 (1923). {377} Gilman, Perkins, *J. Am. Chem. Soc.* 47, 251 (1925). {378} Földi, *Ber.* 60, 650 (1927). {379} Clemo, Perkin, *J. Chem. Soc.* 121, 644 (1922). {380} Clemo, Tenniswood, *J. Chem. Soc.* 1931, 2559.

{381} Tipson, Creteher, *J. Am. Chem. Soc.* 64, 1162 (1942). {382} Gilman, Beaber, *J. Am. Chem. Soc.* 45, 841 (1923). {383} Perkin, Clemo (to British Dyestuffs Corp.), *Brit.* 193,618, March 22, 1923, *Cent.* 1925, I 899; *C.A.* 17, 3510 (1923). {384} Ashworth, Burkhardt, *J. Chem. Soc.* 1928, 1798. {385} Johnson, Schwartz, Jacobs, *J. Am. Chem. Soc.* 60, 1883 (1938). {386} Bert, *Compt. rend.* 213, 1015-1016 (1941); *C.A.* 37, 4049 (1943). {387} Puyal, Montagne, *Bull. soc. chim.* (4) 27, 862 (1924). {388} von Kereszty, Wolf, *Ger.* 387,063, Jan. 7, 1924; *Cent.* 1924, II 403, not in *C.A.* {389} Dewey, Witt, *Ind. Eng. Chem., Anal. Ed.* 14, 648 (1942). {390} Sprinson, *J. Am. Chem. Soc.* 63, 2250 (1941).

{391} Bickel, French, *J. Am. Chem. Soc.* 48, 749 (1926). {392} Grandière, *Bull. soc. chim.* (4) 35, 189 (1924). {393} Dersin, *Ber.* 54, 3158 (1921). {394} Smith, Platon, *Ber.* 55, 3151 (1922). {395} Wenker, *J. Am. Chem. Soc.* 59, 422 (1937). {396} Carelli, Raeciu, *Atti acca.* I 358-803 (1934); *Cent.* 1934, II 2823, [*C.A.* 29, 622 *Chem. Soc.* 50, 1409-1410 (1934)]. {399} Bennett, {400} Sah, Tao, *Rec. trav. chim.* 58, 14-15 (1930).

{401} Murray, *J. Council Sci. Ind. Research* 17, 213-221 (1944); *C.A.* 39, 2283 (1945). {402} Reed (to C. L. Horn) U.S. 2,378,104, June 12, 1945; *C.A.* 30, 4088 (1945). {403} Goldblatt, Chiesman, *Brit. J. Ind. Med.* 1, 207-213 (1944); Goldblatt, *Brit. J. Ind. Med.* 1, 213-223 (1944); *C.A.* 39, 5359 (1945). {404} Porret, *Helv. Chim. Acta*, 27, 1321-1328 (1944); *C.A.* 39, 4789 (1945). {405} Michael, Weiner, *J. Am. Chem. Soc.* 58, 1003 (1936).

3:5555 1,1,1,2-TETRACHLOROETHANE  $\text{Cl}_2\text{CH}_2\text{CCl}_2$

(Acetylidene tetrachloride)

(*unum*-Tetrachloroethane)

[For reactn. of  $\bar{C}$  with acetylene + cat. to yield 1,2-dichloroethylene (3:5030) with 1,1,2-trichloroethylene as by-product see (15); for reactn. of  $\bar{C}$  with 1,2-dichloroethylene +  $AlCl_3$  to yield a pentachlorobutane, b.p. 76-77.9° at 10 mm.,  $D_4^{22} = 1.611$ ,  $n_D^{22} = 1.5518$ , see (16); for reactn. of  $\bar{C}$  with  $C_6H_5MgBr$  in toluene see (17).]

3:5555 (1) Henne, Hubbard, *J. Am. Chem. Soc.* 59, 404-406 (1936). (2) Kharasch, Norton, Mayo, *J. Org. Chem.* 3, 48-51 (1938). (3) Phillips, Davies, Mumford, *J. Chem. Soc.* 1929, 548. (4) Mann, Pope, *J. Chem. Soc.* 124, 597 (1922). (5) Nicodemus, *J. prakt. Chem.* (2) 83, 318 (1911). (6) Parkhurst (to Stand. Oil Co.), U.S. 1,948,045, Feb. 20, 1934; *Cent.* 1934, II 863; *C.A.* 28, 2921 (1934). (7) Kline (to du Pont Rayon), U.S. 2,612,944, June 2, 1936; *Cent.* 1937, I 478; *C.A.* 30, 5038 (1936). (8) Regnault, *Ann. chim.* (2) 69, 162 (1835). (9) Laurent, *Ann.* 22, 292-305 (1857). (10) I.G., Ger. 530,649, July 31, 1931, *Cent.* 1931, II 1920.

(11) Kaufmann, *Ber.* 55, 258 (1922). (12) Mouneyrat, *Bull. soc. chim.* (3) 19, 499-500 (1898). (13) Kokatnur, *J. Am. Chem. Soc.* 41, 122-123 (1919). (14) Prins, *Rec. trav. chim.* 45, 80-81 (1926). (15) Wiegand (to Chem. Fabrik von Heyden), Ger. 566,034, Dec. 14, 1932; *Cent.* 1933, I 1350; Ger. 567,272, Dec. 30, 1932; *Cent.* 1933, I 1842. (16) Prins, *Rec. trav. chim.* 56, 123-124 (1937). (17) Berj, *Bull. soc. chim.* (4) 41, 1173-1174 (1927).

3:5570 *d,l*- $\alpha$ -CHLORO-*n*-BUTYRYL CHLORIDE  $C_4H_7OCl_2$  Beil. II - 277  
 $CH_3CH_2CH(Cl)C(=O)Cl$  II<sub>1</sub>-(123)  
 $\begin{array}{c} Cl \\ | \\ Cl \end{array}$  II<sub>2</sub>-  
 B.P. 120-132° (1)  $D_4^{17} = 1.257$  (1)  
 62-63° at 70 mm. (2)  
 51-52° at 41 mm. (2)

[For prepn. of  $\bar{C}$  from  $\alpha$ -chloro-*n*-butyric acid (3:9130) with  $SOCl_2$  see (2); for formn. of  $\bar{C}$  from *n*-butyryl chloride (3:7370) with  $SO_2Cl_2$  + dibenzoyl peroxide in  $CCl_4$  (15%  $\bar{C}$  + 55%  $\beta$ - and 30%  $\gamma$ -isomers) see (3).]

$\bar{C}$  on hydrolysis with aq. yields  $\alpha$ -chloro-*n*-butyric acid (3:9130) q.v.

3:5570 (1) Markownikow, *Ann.* 153, 241 (1870). (2) Blaise, *Bull. soc. chim.* (4) 15, 668 (1914). (3) Kharasch, Brown, *J. Am. Chem. Soc.* 62, 925-929 (1940).

3:5570  $\beta$ -CHLOROPROPIONALDEHYDE  $C_3H_5OCl$  Beil. I - 632  
 (3-Chloropropanal-1,  $CH_3CH_2CH(Cl)CHO$  I<sub>1</sub>-  
 acrolein hydrochloride)  $\begin{array}{c} Cl \\ | \end{array}$  I<sub>2</sub>-(690)  
 B.P. 130-131° (1)  $D_4^{15} = 1.208$  (1)  $n_D^{15} = 1.475$  (1)  
 125-130° (2)  
 50° at 60 mm. (3)  
 40-44° at 18 mm. (4)  
 40° at 19 mm. (1)  
 40-50° at 10 mm. (2)

Liquid, insol. aq., sol. alc. or ether. —  $\bar{C}$  readily polymerizes (see below).

### PREPARATION OF $\bar{C}$

[For prepn. of  $\bar{C}$  from acrolein (1:6115) with dry  $HCl$  gas at -10 to -15° (yields: 87% (5), 65% (4), (6) (7) (8) (9) (10) see indic. refs.; note that since  $HCl$  is present much of the prod. may appear as the trimer (see below), for prepn. of  $\bar{C}$  from its trimer (see below) by distillation at ord. press. see (1), for prepn. of  $\bar{C}$  from 1,2-dichloropropene-1 (3:5280) by cat. vapor-phase hydration see (20).]



tives) formerly (4) regarded as *cis* and *trans* stereoisomers of  $\bar{C}$  may very probably be  $\bar{C}$  and its synionic isomer (3:7480).

[For prepn. of  $\bar{C}$  from 1,2,3-trichloro-2-methylpropane (3:5885) by dehydrochlorination with quinoline (73-85% yield) see (7).]

[For prepn. of  $\bar{C}$  from 1,1-dichloro-2-methylpropene-2 (3:7480) by hgt. under reflux see (2); for formn. of  $\bar{C}$  (together with other products) from 2-methylpropene-1 (isobutylene) (60% yield (5)) (1) +  $Cl_2$ , or from 3-chloro-2-methylpropene-1 (isohutenyl chloride) (3:7145) with  $Cl_2$  (1 mole) +  $NaHCO_3$  (1.5 moles) at 0° (2) see indic. refs.; for formn. of  $\bar{C}$  (20% yield (6)) (together with other products) from 1,3-dichloro-2-methylpropanol-2 (3:5977) + strong oxygen acids see (6); for formn. of  $\bar{C}$  (46% yield (3)) from 1,3-dichloro-2-methylpropanol-2 (3:5977) by hgt. with  $P_2O_5$  for 2 hrs. at 110-115° see (3).]

$\bar{C}$  on hydrolysis with aq. +  $CaCO_3$  (2) (4) or aq. +  $MgO$  (4) gives (2) (3) (46% yield (4)) 1-chloro-2-methylpropen-1-ol-3 (3-chloro-2-methylallyl alc.) (3:8340) q.v.

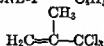
$\bar{C}$  with  $O_3$  followed by hydrolysis yields (2) (3) (5) chloroacetone (3:5425).

$\bar{C}$  treated with  $Cl_2$  in the dark at 0° for 37 hrs. yields (4) 1,1,2,3-tetrachloro-2-methylpropane (3:6165) + other products.

$\bar{C}$  with cuprous cyanide refluxed 9-10 hrs. gives (67% yield (7)) 4-chloro-3-methylbuten-3-nitrile-1, h.p. 70-73° at 10 mm.,  $D_4^{20} = 1.0856$ ,  $n_D^{20} = 1.4643$  (7); this product on hydrolysis with hot conc.  $HCl$  for 2 hrs. gives (7) 4-chloro-3-methylbuten-3-oic acid-1, m.p. 35° (corresp. phenylhydrazide, m.p. 147-148°).

3:5590 (1) Pogorshelski, *J. Russ. Phys.-Chem. Soc.* 36, 1129-1184 (1904); *Cent.* 1905, 1 668, (2) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, 11 4223; *C.A.* 33, 4190 (1939). (3) D'yakonov, *J. Gen. Chem.* 10, 1000-1001 (1936). (4) Rogers, Nelson, *J. Am. Chem. Soc.* 58, 1258-1264 (1936). (5) Development Co., U.S. 2,042,223, 2,042,222, May 26, 1936; *Cent.* 1937, 1274; *C.A.* 30, 4875 (1936). (7) Mooradian, Cloke, *J. Am. Chem. Soc.* 68, 785-789 (1946).

3:5605 3,3,3-TRICHLORO-2-METHYLPROPENE-1  $C_4H_5Cl_3$  Beil. S.N. 11  
(1,1,1-Trichloro-2-methylpropene-2)



B.P. 132° (1)

$D_4^{20} = 1.293$  (1)

$n_D^{20} = 1.479$  (1)

Note:  $\bar{C}$  readily undergoes allylic transposition so that in reactns. of  $\bar{C}$  products derived from the isomeric 1,1,3-trichloro-2-methylpropene-1 (3:5025) may be expected (1) (2) (3) (4).

[For prepn. of  $\bar{C}$  (yield: 30-43% (4), 15% (1)) from  $\beta,\beta,\beta$ -trichloro-*ter*-butyl alc. ("Chlore-tone") (3:2662) by hgt. to 200° with  $P_2O_5$  and dimethylaniline (1) or quinoline (4) see indic. refs.] [A 57% yield of the isomeric 1,1,3-trichloro-2-methylpropene-1 (3:5025) together with some  $\alpha$ -chloroisohutyric acid (3:0235) is separated from  $\bar{C}$  by redistillation (1).]

$\bar{C}$  on hydrolysis by hoihg. 1 dny with aq.  $Na_3PO_4$  gives (60% yield (2)) 3,3-dichloro-2-methylpropen-2-ol-1, h.p. 78-79°,  $D_4^{20} = 1.298$ ,  $n_D^{20} = 1.493$  (*p*-nitrobenzoate, m.p. 91°, *N*-phenylcarbamate, m.p. 64° (2)).

$\bar{C}$  on hgt. with  $NaOAc$  +  $AcOH$  gives (2) 3,3-dichloro-2-methylpropen-2-yl acetate, b.p. 79° at 12 mm.,  $D_4^{20} = 1.257$ ,  $n_D^{20} = 1.4718$  (2). [With hoihg.  $NaOH$  this regenerates the corresp. alc. (2).]

$\bar{C}$  with  $NaOEt$  gives in the cold 70% yield (2) of 3,3-dichloro-2-methylpropen-2-yl ethyl ether, h.p. 56° at 12 mm.,  $D_4^{20} = 1.1285$ ,  $n_D^{20} = 1.4610$  (2).

$\bar{C}$  in AcOH treated with  $O_3$ , then hydrolyzed, gives (70% yield)  $\alpha, \alpha, \alpha$ -trichloroacetone (3:5620), b.p. 133-134° (1).

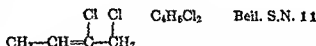
[For behavior of  $\bar{C}$  with  $PCl_5$ , with HF, or with HF + anisole see (4).]

⑥ 2,3-Dibromo-1,1,1-trichloro-2-methylpropane: m.p. 34° (1). [From  $\bar{C}$  +  $Br_2$  without solvent; crude prod. recrystd. from alc. at -10° (1); cf., however, (4).]

⑦ 3,3-Dichloro-2-methylpropen-2-yl  $\beta$ -nitrobenzoate: m.p. 01° (2). [From  $\bar{C}$  on boilg. with dil. alc. soln. of K  $\beta$ -nitrobenzoate (2).]

3:5605 (1) Jacob, *Bull. soc. chim.* (5) 7, 581-586 (1940). (2) Kirmann, Jacob, *Bull. soc. chim.* (5) 7, 586-593 (1940). (3) Kirmann, Jacob, *Compt. rend.* 203, 1528-1529 (1936). (4) Price, Marshall, *J. Org. Chem.* 8, 532-535 (1943)

3:5615 1,2-DICHLOROBUTENE-2  
(high-boilg. stereoisomer)



B.P. 132-134° at 762 mm. (1)  
125-127° (2)

$D_4^{20} = 1.1597$  (2)  $n_D^{20} = 1.4590$  (2)  
 $D_4^{18} = 1.1601$  (2)  $n_D^{18} = 1.4635$  (2)  
 $D_4^{16} = 1.1771$  (1)  $n_D^{16} = 1.4710$  (1)

[See also low-boilg. stereoisomer (3:5360).]

[For prepn. of  $\bar{C}$  (together with its stereoisomer (3:5360)) from 1,2,3-trichlorobutane (3:5935) with KOH at 150° (2), or from 2,2-dichlorobutane (3:7415) or 2,3-dichlorobutane (3:7615) with alc. KOH (5), see indic. refs.; for formn. of  $\bar{C}$  (together with its stereoisomer and also 2,4-dichlorobutene-2 (3:5550)) from 2-chlorobutene-2 (3:7105) by actn. of  $Cl_2$  at 350° see (3).]

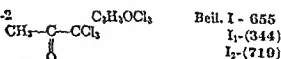
$\bar{C}$  with 1 mole  $Cl_2$  + 1.5 moles  $NaHCO_3$  at 0° gives (100% yield (4)) 1,2,2,3-tetrachlorobutane (3:9078).

$\bar{C}$  on hydrolysis by htg. with 2 pts. aq. + 1 mole powdered  $CaCO_3$  at 70° for 4 hrs. gives (1) a mixt. of about equal parts of 2-chlorobuten-2-ol-1 (3:8240) and (by allylic transposition) 3-chlorobuten-3-ol-2 (3:9115).

$\bar{C}$  on oxidn. with  $KMnO_4$  in acetone gives (1) chloroacetic acid (3:1370) + AcOH (1:1010) + HCl. —  $\bar{C}$  in  $CCl_4$  at -17° treated with  $O_3$  followed by aq. gives acetaldehyde (1:0100).

3:5615 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 7, 658-662 (1937); *Cent.* 1937, II 371; *C.A.* 31, 5754 (1937). (2) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 6, 1553-1558 (1936); *Cent.* 1937, I 3786; *C.A.* 31, 2165 (1937). (3) N. V. Bataafsche Petroleum Maatschappij, *Brit.* 468,016, July 22, 1937, French 810,112, Mar. 15, 1937; *Cent.* 1937, II 4102. (4) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *Cent.* 1939, II 4222; *C.A.* 33, 4190 (1939). (5) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 7, 663-666 (1937); *Cent.* 1937, II 371; *C.A.* 31, 5764 (1937).

3:5620 1,1,1-TRICHLOROPROPANONE-2  
( $\alpha, \alpha, \alpha$ -Trichloroacetone;  
methyl trichloromethyl ketone)



B.P. 134° (1) (3)  
133-134° (2)  
60° at 54 mm. (1)  
57° at 48 mm. (1)  
27.5-28° at 10 mm. (3)

$D_4^{20} = 1.435$  (3)  $n_D^{20} = 1.4602$  (3)  
 $D_4^{17.1} = 1.4380$  (3)

Limpid colorless liq. with faintly camphoraceous odor. — Insol. aq., but volatile with steam (3). —  $\bar{C}$  is not lachrymatory.

[For prepn. from 1,1,1-trichloro-2-methylpropene-2 (3:5605) with  $O_3$  in AcOH, followed by hydrolysis (76% yield) see (2); from corresp. alc., 1,1,1-trichloropropanol-2 (3:0846), by oxidn. with  $K_2Cr_2O_7/H_2SO_4$  see (3); from 2-trichloromethyl-2,4,4-trimethyl-1,3-dioxolone-5 (Beil. XIX-1-(656)) by hydrolytic cleavage with AcOH/HCl (60% yield) see (1); for formn. of  $\bar{C}$  (together with other prodn.) from propanol-2 (1:6135) with  $Cl_2$  (4), from chloroacetone (3:5425) with  $Cl_2$  at  $30-40^\circ$  (5), or from trichloroacetyl chloride (3:5420) with MoZnI (1) see indic. refs. — Note that the prod. from chloral + diazomethane, formerly supposed (6) to have been  $\bar{C}$ , has since been shown (7) (8) to be 3,3,3-trichloro-1,2-epoxypropane (3:5700) ("γ,γ,γ-trichloropropylene oxide").]

[ $\bar{C}$  on reduction with  $Al(C_2H_5)_3.H_2O$  in ether (9) or with fused  $Al(OEt)_3$  in abs. alc. under  $H_2$  or  $N_2$  (10) gives yields: 67% (10), 65% (9)] 1,1,1-trichloropropanol-2 (3:0846).]

[ $\bar{C}$  resists further chlorination; e.g.,  $\bar{C}$  with  $SO_2Cl_2$  (1 mole) on protracted htg. at  $180^\circ$  yields (3) 1,1,1,3-tetrachloropropanone-2 (3:6085), b.p.  $71-72^\circ$  at 13 mm., hydrate, m.p.  $65^\circ$  (3).]

[ $\bar{C}$  with diazomethane in dry ether gives (83% yield (3)) 1,1,1-trichloro-2-methyl-2,3-epoxypropane, b.p.  $51^\circ$  at 10 mm., m.p.  $53-54^\circ$  (3).]

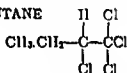
⑤ Cleavage with aq. alkali:  $\bar{C}$  with aq. alk. even in cold splits almost instantly (1) (2) into chloroform (3:5050) and acetic acid (1:1010).

⑥ 1,1,1-Trichloropropanone-2 semicarbazone: m.p.  $140^\circ$  dec. (on Hg bath) (1) (11).

[From  $\bar{C}$  with semicarbazide HCl in pres. of NaOAc, or with free semicarbazide (11).]

3:5620 (1) Iblaise, *Bull. soc. chim.* (4) 15, 731-737 (1914); *Compt. rend.* 155, 1253 (1912). (2) Jacob, *Bull. soc. chim.* (5) 1, 214-216 (1912). (3) *Monatsh.* 59, 214-216 (1928). (4) *Cent.* 1922, IV 012. (5) *Beck, Ber.* 42, 2561-2562. (6) *Schlotterbeck, Ber.* 42, 2561-2562. (7) *Z. angew. Chem.* 40, 1090-1100 (1927). (8) Meerwein, Hinz, Majert, Sönke, *J. prakt. Chem.* (2) 147, 236-237 (1930). (9) Meerwein, Schmidt, *Ann.* 444, 233-234 (1925). (10) Iblaise, *Bull. soc. chim.* (4) 17, 428 (1915); *Compt. rend.* 156, 1551 (1913).

### 3:5622 1,1,1,2-TETRACHLOROBUTANE


 $C_4H_2Cl_4$ 

Bell. S.N. 10

 B.P.  $134-135^\circ$  at 742 mm. (1)

 $D_{20}^{20} = 1.3932$  (1)

 $n_D^{25} = 1.4926$  (1)

[For prepn. of  $\bar{C}$  from 1,1,1-trichlorobutanol-2 (3:5955) with conc. HCl +  $ZnCl_2$  on stlg. at room temp. 1 hr. (yield not stated) see (1).]

3:5622 (1) Gilman, Abbott, *J. Org. Chem.* 8, 228 (1913).

### 3:5625 ETHOXALYL CHLORIDE


 $C_4H_5O_2Cl$ 

Bell. II - 541

 $\text{II}_1$ -(234)

 $\text{II}_2$ -(508)

 B.P.  $136-138^\circ$ 

(1)

 $D_4^{20} = 1.2231$  (2)

 $135-136^\circ$ 

(2)

 $1.2226$  (3)

 $135^\circ$ 

(3)

 $134-135^\circ$ 

(4)

 $133-135^\circ$  at 760 mm. (14)

 $30^\circ$  at 10 mm. (2)

Colorless mobile liq. with penetrating odor. —  $\bar{C}$  fumes in air and gradually deposits hydrated oxalic acid (1:0445) (17). —  $\bar{C}$  as such is insol. in aq. but rapidly hydrolyzes with formn. of HCl and ethyl hydrogen oxalate, the latter in turn being converted to oxalic acid (1:0445) + EtOH.

[For prepn. of  $\bar{C}$  from diethyl oxalate (1:1055) with  $PCl_5$  (yields: 80–90% (5), 84% (6), 80% (7), (8) (9) (10) (11) (34) see indic. refs.; note that this mode of prepn. has been shown (4) to comprise two distinct and successive reactions: first the formn. of ethyl  $\alpha,\alpha$ -dichloro- $\alpha$ -ethoxyacetate,  $Cl_2C(OEt).COOEt$  [Beil. II-543, II<sub>1</sub>-(236)], b.p. abt. 85° at 10 mm.,  $D_4^{20} = 1.23155$  (2); and second, the pyrolysis of this product by repeated distillation (13) or increased temp. (especially in the pres. of catalysts such as salts of Fe or Pt (5) (12)) yielding  $\bar{C}$  + ethyl chloride (3:7015).]

[For prepn. of  $\bar{C}$  from ethyl hydrogen oxalate [Beil. II-535, II<sub>1</sub>-(232), II<sub>2</sub>-(504)] with  $SOCl_2$  (yields: 78% (14), 72% (15)) or with  $PCl_5$  (3) see indic. refs. (note that the initial ethyl hydrogen oxalate is readily obtd. from anhydrous oxalic acid (1:0535) with diethyl oxalate (1:1055) by htg. 3 hrs. (32% yield (15)) (18) or by distn. with EtOH and  $CCl_4$  as directed (61% yield (16))); for prepn. of  $\bar{C}$  from K ethyl oxalate with  $POCl_3$  or  $PCl_5$  (17) (3) or with  $SOCl_2$  (60–70% yield (24)) see indic. refs. (note that K ethyl oxalate can readily be prepd. in 95–97% yield from diethyl oxalate (1:1055) by digestion with aq. KOAc (24)).]

[For prepn. of  $\bar{C}$  from oxalyl (di)chloride (3:5060) with EtOH (1:6130) by reactn. of one acid chloride group but not the other (60% yield) see (25).]

[ $\bar{C}$  on passing through tube at 200° loses CO yielding (19) ethyl chloroformate (3:7295).]

[ $\bar{C}$  with EtOH (1:6130) reacts normally yielding (17) diethyl oxalate (1:1055); for reactn. of  $\bar{C}$  with cellulose see (25).]

[ $\bar{C}$  with diethyl sodiomalonate in ether gives (20) (12) a mixt. of triethyl oxalomalonate [Beil. III-850, III<sub>1</sub>-(292)] and tetraethyl dioxalomalonate [Beil. III<sub>2</sub>-(199)];  $\bar{C}$  with ethyl sodio-cyanoacetate in ether gives (21) (22) diethyl oxalo-cyanoacetate [Beil. III-850], m.p. 98° (22), 96° (21);  $\bar{C}$  with diethyl methyl sodio-malonate gives (23) diethyl oxalo-methyl-malonate; many other analogous condensations cannot be included here.]

[ $\bar{C}$  with aromatic hydrocarbons in the pres. of  $AlCl_3$  undergoes reactn. of the Friedel-Crafts type, and this procedure has been widely studied as a means of introduction of the  $-CO.COOC_2H_5$  group: e.g.,  $\bar{C}$  with  $C_6H_6$  +  $AlCl_3$  in nitrobenzene +  $CS_2$  gives (26) ethyl benzoylformate (ethyl phenylglyoxylate) [Beil. X-657, XI<sub>1</sub>-(314)], b.p. 256–257°; for corresp. analogous reactn. with toluene (1:7405) (27), *m*-xylene (1:7420) (27), cumene (1:7440) (9), pseudocumene (1:7470) (27), or mesitylene (1:7455) (27) (1) see indic. refs.]

$\bar{C}$  with  $NH_3$  in alc. gives (17) ethyl oxamate,  $NH_2.CO.CO.OC_2H_5$  [Beil. II-544, II<sub>1</sub>-(236), II<sub>2</sub>-(509)], lfts. from hot alc., m.p. 114°. — Similarly  $\bar{C}$  with aniline should yield ethyl oxanilate,  $C_6H_5.NH.CO.CO.OC_2H_5$  [Beil. XII-282, XII<sub>1</sub>-(206)], tbs. or pr. from alc., ndls. from hot aq., m.p. 66–67°;  $\bar{C}$  with phenylhydrazine should yield  $\beta$ -(ethoxalyl)-phenylhydrazine,  $C_6H_5.NH.NH.CO.CO.OC_2H_5$  [Beil. XV-264], lfts. from alc., m.p. 119°.

$\bar{C}$  with urea (2 moles) reacts vigorously at room temp. as a normal acid chloride yielding (28) ethyl oxalurate,  $NH_2.CO.NH.CO.CO.OC_2H_5$  [Beil. III-65, III<sub>2</sub>-(54)], ndls. from ether, m.p. 184–185°. — Note, however, that  $\bar{C}$  with *N*-phenylurea on htg. evolves CO +  $C_2H_5Cl$  (3:7015) and yields (29) a mixt. of ethyl  $\alpha$ -phenylallophanate,  $C_6H_5.NH.CO.NH.COOC_2H_5$  [Beil. XI-359, XII<sub>1</sub>-(234)], ndls. from boilg. alc., m.p. 106° (30), and *N*-phenyl-parabanic acid (oxalyl *N*-phenylurea) [Beil. XXIV-454, XXIV<sub>1</sub>-(405)], lfts. from alc., m.p. 208° (29). —  $\bar{C}$  with *N,N'*-diphenylurea in  $C_6H_6$  on htg. evolves  $C_2H_5Cl$  (3:7015) and yields (29) *N,N'*-diphenylparabanic acid (oxalyl *N,N'*-diphenylurea) [Beil. XXIV-455, XXIV<sub>1</sub>-(405)], ndls. from alc., m.p. 204°. —  $\bar{C}$  with *N,N'*-dimethylurea (2 moles)

reacts vigorously giving (80% yield (31)) *N,N'*-dimethylparahanic acid [Beil. XXIV-453, XXIV<sub>1</sub>-(404)], m.p. 154°.

[ $\bar{C}$  with  $RMgX$  cpds. gives (32) disubstituted glycolic acids ( $R_2C(OH)COOH$ ) and/or ethoxalyl esters of disubstituted ethyl glycolates,  $R_2C(O.CO.COOC_2H_5)$  ( $COOC_2H_5$ ); similarly  $\bar{C}$  with diethylcadmium gives (63% yields (33)) ethyl  $\alpha$ -ethyl- $\alpha$ -hydroxy-n-butyrate (ethyl  $\alpha,\alpha$ -diethylglycolate).]

(1) *Ann.* 254, 20, 27 (1889). (3) *Mol.* 2160 (1886). (5) *Blaise, Bull.* 47-49 (1927). (7) *Bert, Bull.* 2160 (1886). (9) *Bert, Bull.* 373-378 (1905). (12) *Scholl, Egerer, Ann.* 397, 678 (1928). (14) *Diels, Nawall. soc. chim.* (4) 41, 537-540 (1927). (16) *Contzen-Crewet, Bull. soc. chim. Belg.* 35, 167-170 (1926). (17) *Henry, Ber.* 4, 599-601 (1871). (18) *Fourneau, Sabetay, Bull. soc. chim.* (4) 43, 860 (1928). (19) *Grassi, Gazz. chim. ital.* 27, I 31-32 (1897). (20) *von Auwers, Auffenberg, Ber.* 51, 1103-1106 (1918).

(21) *Bertini Gazz. chim. ital.* 31, I Adickes, *Brun. Ber.* 63, 1532-6 (1897). (27) 3 (1871). (29) 45-345 (1897). 48-953 (1903). 8,532, Oct. 29, 1942; *C.A.* 33, 378 (1944).

3:5630 1,1,2-TRICHLOROPROPANE  $CH_3CH(Cl).CHCl_2$   $C_3H_5Cl_3$  Beil. I-106  
( $\alpha$ -Chloropropylidene (di)-chloride)  $I_1$ —  
 $I_2$ —

B.P. 135-137° (1) cf. (2)  
132° (3)

$D_4^{16} = 1.353$  (1)

[For prepn. from 1,2-dichloropropane (propylene dichloride) (3:5200) by chlorination in presence of iron and ultra-violet light at 10-40°, or without ultra-violet light above 50°, see (4), or with  $SO_2Cl_2$  in pres. of organic peroxides see (6) (7).]

$\bar{C}$  htd. with aq. or alc. alk. splits out HCl yielding (5) 1,1- (3:5120), h.p. 78°.

(1) *Ann.* 21, 620 (1899). (2) *V.* 3. (4) *Levine, C.* (to du Pont). *Chem. Soc.* 61, 27, 1945; *C.A.* *chim.* 471, 30.

3:5633 3-CHLORO-2-PROPENE-1  
(1-Chloro-2-(chloromethyl)- $\gamma,\gamma$ -dichloroisobutylene)



B.P. M.P.  
138-138.3° (9) -15°  
30-31° at 9 mm. (1)

Colorless oil with faintly halogen-

[For prepn. of  $\bar{C}$  from *tris*-(chloromethyl)acetic acid (itself obtd. in quant. yield by conc.  $\text{HNO}_3$  oxidn. (9) of 3-chloro-2,2-bis-(chloromethyl)propanol-1 = pentaerythrityl tri-chlorohydrin (9)) by combine decarboxylation and dehydrochlorination in boilg. quinoline (75-85% yield) see (9).]

[For formn. of  $\bar{C}$  (40% yield (2) together with other products (2) (3)) from 2-methylpropene-1 (isobutylene) with  $\text{Cl}_2$  (2) (3) or from 3-chloro-2-methylpropene-1 (isobutenyl chloride) (3:7145) with  $\text{Cl}_2$  (1 mole) +  $\text{NaHCO}_3$  (1.5 moles) at  $0^\circ$  see (2) (4) see indic. refs.; for formn. of  $\bar{C}$  (together with other products) from 1,2,3-trichloro-2-methylpropane (3:5885) by pyrolysis at 450-550° see (5); for formn. of  $\bar{C}$  (together with 1,3-dichloro-2-(chloromethyl)propene-1 (3:9066)) from 1,3-dichloro-2-nitro-2-(chloromethyl)propane with  $\text{Na/Hg}$  see (1); for prepn. of  $\bar{C}$  (80% yield (6) together with 20% yield 1,3-dichloro-2-methylpropene-1 (3:5590)) from 1,3-dichloro-2-methylpropanol-2 (3:5977) by actn. of strong oxygen acids see (6).]

$\bar{C}$  on cat. hydrogenation using Pt black yields (1) 1,3-dichloro-2-methylpropane (3:7060), but  $\bar{C}$  in alc. on bodg. with Zn dust gives (75% yield (3)) isobutylene, b.p.  $-6^\circ$ .

$\bar{C}$  with  $\text{O}_3$  gives (2)  $\alpha,\alpha'$ -dichloroacetone (3:0563).

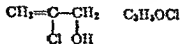
$\bar{C}$  treated with  $\text{Cl}_2$  in the dark at  $0^\circ$  yields (5) 1,2,3-trichloro-2-chloromethylpropane (3:6335). —  $\bar{C}$  treated with  $\text{Br}_2$  in  $\text{CHCl}_3$  yields (1) 1,2-dibromo-3-chloro-2-(chloromethyl)propane, colorless odorless oil, b.p.  $140^\circ$  at 10 mm. (1); note, however, failure to react with  $\text{Br}_2$  recorded later (3).

$\bar{C}$  with aq. alk. as specified (7) yields 2,3-epoxy-2-chloromethylpropanol-1, b.p.  $55^\circ$  at 1 mm. (7). [For similar reactns. cf. (8).]

$\bar{C}$  on hydrolysis with aq.  $\text{CaCO}_3$  refluxed 2 hrs. gives (36% yield (9)) 2-(hydroxymethyl)propen-2-ol-1, b.p.  $125-126^\circ$  at 18 mm.,  $D_4^{20} = 1.0791$ ,  $n_D^{20} = 1.4758$  (9).

3:5633 (1) Kleinfeller, *Ber.* 62, 1505 (1929). (2) D'yakonov, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 9, 1234-1261 (1939), *C.A.* 34, 710 (1940). (3) D'yakonov, *J. Gen. Chem. (U.S.S.R.)* 10, 402-413 (1940), *C.A.* 34, 7661 (1940). (4) Engs, Groll, Fairbairn (to Shell Development Co.), U.S. 2,189,800, Feb. 13, 1940; *C.A.* 34, 4079 (1940). (5) Rogers, Nelson, *J. Am. Chem. Soc.* 54, 1029-1031 (1936). (6) Groll, Burgen (to Shell Development Co.), U.S. 2,042,223, U.S. 2,042,222, May 26, 1936, *Cent.* 1937, 1 1274, *C.A.* 30, 4875 (1936). (7) Groll, Hearne (to Shell Development Co.), U.S. 2,070,990, Feb. 16, 1937; *Cent.* 1937, II 2133, *C.A.* 31, 2612 (1937). (8) Hearne, de Jong, *Ind. Eng. Chem.* 33, 910-913 (1941). (9) Mooradian, Cloke, *J. Am. Chem. Soc.* 67, 912-914 (1945).

3:5635 2-CHLOROPROPEN-2-OL-1  
(2-Chloropropen-1-ol-3;  
 $\beta$ -chloroallyl alcohol)



$\text{C}_3\text{H}_5\text{OCl}$  Beil. I-439  
I<sub>1</sub>—  
I<sub>2</sub>—

B.P.  $136-140^\circ$  cor. (1)  
 $136^\circ$  (2)

$D_4^{20} = 1.164$  (2)

Note that  $\bar{C}$  is the true  $\beta$ -chloroallyl alcohol; care must be taken to avoid confusion with 3-chloropropen-2-ol-1 ( $\gamma$ -chloroallyl alcohol) (3:5820) whose derivatives have often been designated in the literature as  $\beta$ -chloroallyl derivatives; see also the warning note under  $\gamma$ -chloroallyl chloride (3:5290).

[For prepn. of  $\bar{C}$  from 2,3-dichloropropene-1 (3:5190) by hydrolysis of the reactive halogen atom with hot dil. aq. alk. see (2); from 2-chloro-3-iodopropene-1 by hydrolysis of the iodine atom with hot dil. aq.  $\text{KOH}$  or with silver oxide see (1); from butadiene-1,2-(allene) with  $\text{HOCl}$  see (3).]

Colorless liq. with faint odor;  $\bar{C}$  does not have the violent vesicant action on skin shown by the isomeric  $\gamma$ -chloroallyl alc. (3:5820).

$\bar{C}$  readily dissolves in conc.  $H_2SO_4$  with evolution of  $HCl$  gas; after pouring onto ice and distilling acetol (hydroxyacetone) (1:5455) is obt'd. (2).

[ $\bar{C}$  with  $PBr_3$  yields (2) 3-bromo-2-chloropropene-1 ( $\beta$ -chloroallyl bromide) [Beil. I-201, I<sub>1</sub>-(171)], b.p.  $121^\circ$  (2),  $110-120^\circ$  (4).]

[ $\bar{C}$  yields by suitable treatment (no details (2))  $\beta$ -chloroallyl acetate [Beil. II-136], b.p.  $145^\circ$  (2). — For esters of  $\bar{C}$  with monocarboxylic acids (5), saturated polycarboxylic acids (6), and halogenated acids (7), and for copolymerization of certain esters of  $\bar{C}$  with styrene (8) see indic. refs.]

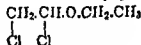
3:5635 (1) van Romburgh, *Rec. trav. chim.* 1, 238 (1882). (2) Henry, *Bull. soc. chim.* (3) 21, 526 (1883). (3) Smirnov, *J. Russ. Phys.-Chem. Soc.* 35, 854-872 (1903); *Cent.* 1904, 1 574 (4) von Braun, Köhn, Weismantel, *Ann.* 440, 256 (1926). (5) Coleman, Hadler (to Dow Chem. Co.), U.S. 2,208,960, July 23, 1941. (6) Coleman, Hadler (to Dow Chem. Co.), U.S. 2,159,008, May 23, 1941. (7) Coleman, Hadler (to Dow Chem. Co.), U.S. 2,221,000, May 23, 1941. (8) Zembra (to Dow Chem. Co.), U.S. 2,221,000, May 23, 1941.

### 3:5640 $\alpha,\beta$ -DICHLORODIETHYL ETHER

( $\alpha,\beta$ -Dichloroethyl ethyl ether)



Beil. I-612



I<sub>1</sub>-(328)

I<sub>1</sub>-(676)

B.P.  $140-145^\circ$

(1) (2)

$D_{25}^{23} = 1.174$  (1)

$132-133^\circ$  at 725 mm. (3)

$66-69^\circ$  at 45 mm. (4)

$36-37^\circ$  at 15 mm. (3)

Colorless liq. with sharp odor.

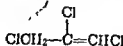
[For prepn. from diethyl ether (1:0110) by chlorination see (4) (1).]

$\bar{C}$  with cold aq. rapidly hydrolyzes yielding chloroacetaldehyde hydrate (3:7212), ethyl alc. (1:6130), and  $HCl$ ; for study of rate at  $20^\circ$  see (5).

$\bar{C}$  in dil. alc. htd. some hrs. at  $60^\circ$  with  $NH_2OH \cdot HCl$  (3 moles) +  $KOH$  (5 moles) soln. evapd., acidified with dil.  $H_2SO_4$ , extracted with ether, ether soln. dried with  $CaCl_2$ , evapd. gives (40% yield (5)) glyoxal dioxime (glyoxime) [Beil. I-701], rec'd. from oil, recrystallized from hot aq., m.p.  $178^\circ$  (5).

3:5640 (1) Lieben, *Ann.* 146, 181-180 (1868). (2) Natterer, *Monatsh.* 5, 490-497 (1881). (3) Mohler, Sorge, *Helv. Chim. Acta* 23, 1209 (1940). (4) Wildman, Gray, *J. Am. Chem. Soc.* 61, 1122-1123 (1939). (5) Hantzsch, Wild, *Ann.* 289, 293 (1896). (6) Mohler, Hartnagel, *Helv. Chim. Acta* 25, 859-863 (1942); *C.A.* 37, 1799 (1943).

### 3:5650 1,2,3-TRICHLOROPROPENE-1



Beil. I-260

I<sub>1</sub>—

I<sub>2</sub>—

B.P.  $142^\circ$  (1)

$D_{20}^{20} = 1.414$  (1)

Liq., insol. aq., cas. sol. alc., ether. [Two geom. stereoisomers are possible but unrecorded.]

[For prepn. of  $\bar{C}$  from 1,2,2,3-tetrachloropropane (3:5895) with alc. alk. see (1).]

[For use in prepn. of unsatd. cellulose ethers see (2); for use in dewaxing mineral oils see (3).]

3:5650 (1) Pfeffer, Fittig, *Ann.* 135, 361-363 (1865). (2) du Pont Co., *Brit.* 429,940, June 11, 1935; *Cent.* 1936, 1 4908; *C.A.* 29, 7073 (1935). (3) Standard Oil Development Co., *French* 790,852, Nov. 28, 1935; *Cent.* 1936, 1 2672; *C.A.* 30, 3223 (1936).

## 3:5655 METHYL DICHLOROACETATE



Beil. II - 203

 $\Pi_1$ — $\Pi_2$ -(196)

B.P. 143.3° at 764.5 mm. (1)

$D_{19}^{19.2} = 1.3808 \text{ (6)}$

143.2° (2)

143° (3) (8)

142-144° (4)

49.8-50° at 20 mm. (5)

[For prepn. of  $\bar{\text{C}}$  from dichloroacetic acid (3:6208) with MeOH + HCl gas (72% yield (3)) (7), with MeOH +  $\text{Et}_2\text{O.BF}_3$  complex (70% yield (3)), with MeOH +  $\text{H}_2\text{SO}_4$  (71.3% yield (3)), or with MeOH itself without any cat. (47-61% yield (3)), or with  $\text{Me}_2\text{SO}_4$  in s.t. at 200° (8) see indic. refs.; for prepn. of  $\bar{\text{C}}$  from dichloroacetamide with  $\text{BF}_3$  in MeOH (57% yield) see (3); for prepn. of  $\bar{\text{C}}$  from chloral (3:5210) (84% yield (9)), chloral hydrate (3:1270) (4), or chloral hydrate diacetate (76% yield (9)) with KCN in MeOH see indic. refs.]

[For reactn. of  $\bar{\text{C}}$  with dimethyl sodio-malonate in MeOH yielding (10) 1,1,2,3,3-penta-(carhomethoxy)propane (Beil. II-880), thls. from MeOH + aq., m.p. 85-86° see (10).]

$\bar{\text{C}}$  on hydrolysis yields dichloroacetic acid (3:6208) q.v. + MeOH (1:6120). [For studies of rate of hydrolysis under various circumstances see (5) (11)]

3:5655 (1) Schiff, *Z. physik. Chem.* 1, 378 (1887). (2) Cheng, *Z. physik. Chem.* B-24, 305 (1934). (3) Toole, Sowa, *J. Am. Chem. Soc.* 59, 1971-1973 (1937). (4) Wallach, *Ann.* 173, 299 (1874). (5) Skrabal, *Monatsh.* 71, 298-308 (1938). (6) Henry, *Compt. rend.* 101, 251 (1885). (7) Müller, *Ann.* 133, 160 (1865). (8) Simon, *Compt. rend.* 176, 585 (1923). (9) Chattaway, Irving, *J. Chem. Soc.* 1929, 1042, 1047. (10) Anschütz, Deschauer, *Ann.* 347, 6-7 (1906). (11) Skrabal, Rückert, *Monatsh.* 50, 369-384 (1928).

3:5660 1,1,3-TRICHLOROPROPANE  
( $\delta$ -Chloropropylidene (di)-chloride) $\text{C}_3\text{H}_3\text{Cl}_3$ 

Beil. I - 106

 $\Pi_1$ — $\Pi_2$ —

B.P. 143-144° (1)

$D_{15}^{18} = 1.351 \text{ (1)}$

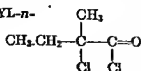
$n_D^{18} = 1.474 \text{ (1)}$

146-148° (2) (3)

$D_{15}^{15} = 1.362 \text{ (3)}$

$\bar{\text{C}}$  with alc. KOH splits out HCl yielding (2) (3) 3,3-dichloropropene-1 (3:5140), b.p. 84°, together with a little 1,3-dichloropropene-1 (3:5280), b.p. 107°.

3:5660 (1) Kirmann, Pacaud, Dosque, *Bull. soc. chim.* (5) 1, 866 (1934). (2) Gustavson, *J. prakt. Chem.* (2) 50, 381-382 (1894). (3) van Romburgh, *Bull. soc. chim.* (2) 37, 100-102 (1882).

3:5670 *d,l*- $\alpha$ -CHLORO- $\alpha$ -METHYL-*n*-  
BUTYRYL CHLORIDE

Beil. II -307

 $\Pi_1$ — $\Pi_2$ —

B.P. 143-144° at 749 mm. (1)

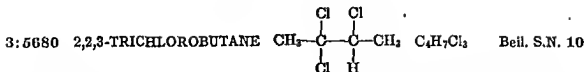
$D_{15}^{14} = 1.187 \text{ (1)}$

[For prepn. of  $\bar{\text{C}}$  from  $\alpha$ -chloro- $\alpha$ -methyl-*n*-butyric acid (3:8718) with  $\text{PCl}_3$  see (1).]

$\bar{\text{C}}$  on hydrolysis with aq. yields (1)  $\alpha$ -chloro- $\alpha$ -methyl-*n*-butyric acid (3:8718) q.v.

3:5670 (1) Servais, *Rec. trav. chim.* 20, 59 (1901).



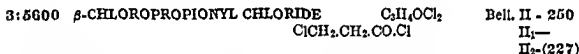


B.P. 143-145°	(2)	$D_4^{20} = 1.2609$	(1)	$n_D^{20} = 1.4045$	(1)
141-143°	(1)	$D_4^{18} = 1.2630$	(2)	$n_D^{18} = 1.4037$	(2)
77-84° at 15 mm.	(2)	$D_4^{12} = 1.33$	(2)	$n_D^{12} = 1.4075$	(2)

[For prepn. of  $\bar{\text{C}}$  (45% yield (2)) from 2-chlorobutene-2 (3:7105) (together with 55% 2,3-dichlorobutene-1 (3:9074)) with  $\text{Cl}_2 + \text{NaHCO}_3$  at 0° (2) (3) or with  $\text{Cl}_2 + \text{SnCl}_4$  in dark (4) see indie. refs.; for formn. of  $\bar{\text{C}}$  (28% yield (1)) from 1,2-dichlorobutane (3:7680) + sl. excess  $\text{Cl}_2$  in dark at -17° (together with 19% 1,2,3-trichlorobutane) (3:5935) see (1); for formn. of  $\bar{\text{C}}$  (18% yield (1)) from 2,3-dichlorobutane (3:7615) + sl. excess  $\text{Cl}_2$  in dark at -17° (together with 36.5% 1,2,3-trichlorobutane (3:5935)) see (1).]

$\bar{\text{C}}$  with solid KOH at 140° loses HCl yielding (1) mixt. of *cis*-2,3-dichlorobutene-2 (3:5500), and *trans* 2,3-dichlorobutene-2 (3:7395).

3:5680 (1) Tishechenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 6, 1553-1558 (1936); *C.A.* 31, 2165 (1937); *Cent.* 1937, I 3786. (2) Tishechenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938); *C.A.* 33, 4190 (1939); *Cent.* 1939, II 4222. (3) du Pont Co., *Brit.* 535,586, April 15, 1941; *C.A.* 36, 1337 (1942). (4) Levine, Cass (to du Pont Co.) U.S. 2,323,227, June 29, 1943; *C.A.* 38, 119 (1944).



B.P. 144.5°	(1)	$D_4^{13} = 1.3307$	(3)
144°	(2)		
143-145°	at 763 mm. (3)		
82-82.5° cor.	at 102 mm. (4)		
87°	at 95 mm. (5)		
53°	at 23 mm. (5)		

Pale yel. liq. with pungent odor, sol. alc., ether, acetone,  $\text{CHCl}_3$  (1).

[For prepn. from  $\beta$ -chloropropionic ac. (3:0460) with  $\text{PCl}_5$  (3) or  $\text{SOCl}_2$  (96% yield (5)) see (3) (2) (5); from propionyl chlorido (3:7170) +  $\text{Cl}_2$  see (4) (9); from phosgene (3:5000) + ethylene +  $\text{AlCl}_3$  see (1) (this method questioned by (6) (7)).]

$\bar{\text{C}}$  over  $\text{Al}_2\text{O}_3$  at 250° loses 1 HCl giving (35% yield (10)) (11) acryloyl chloride (3:7153).

①  $\beta$ -Chloropropionic acid (3:0460): lfts. from lgr. or pet. ether, m.p. 42°. [From  $\bar{\text{C}}$  on boilg. with aq. (1).]

②  $\beta$ -Chloropropionamide: unrecorded.

③  $\beta$ -Chloropropionanilide: cryst. from aq. or MeOH, m.p. 119° (8). [From  $\bar{\text{C}}$  + aniline in acetone; 90% yield (8).]

④  $\beta$ -Chloropropion-*p*-toluidide: cryst. from MeOH, m.p. 121° (8) (2).

3:5690 (1) Peco, *Gazz. chim. ital.* 59, 580-582 (1929). (2) Wolfenstein, Rolle, *Ber.* 41, 736 (1908). (3) Henry, *Compt. rend.* 100, 115 (1885); *J. prakt. Chem.* (2) 31, 127 (1885). (4) Michael, *Ber.* 34, 4047-4048 (1901). (5) Fieser, Seligman, *J. Am. Chem. Soc.* 58, 2484 (1936). (6) Frolich, Wiezevich, *Ind. Eng. Chem.* 24, 16 (1932). (7) Varshavskii, Doroganyevskaya, *Gazz. chim. ital.* 64, 53-59 (1934). (8) Mayer, van Zütphen, Philipps, *Ber.* 58, 869 (1927); Mayer, *Ger.* 415,000, June 13, 1925; *Cent.* 1925, II 1091. (9) Schmidt, Schloffer (to I.G.) *Ger.* 738,398 (1944). (10) Schmidt, Schloffer (to I.G.) *Ger.* 738,398 (1944). (11) Schmidt, Schloffer (to I.G.) *Ger.* 738,398 (1944).

(1936): *Brit.* 333,970,

3:5700 ETHYL CHLOROACETATE  $\text{CH}_3\text{COOC}_2\text{H}_5$   $\text{C}_4\text{H}_7\text{O}_2\text{Cl}$  Beil. II - 197  
 $\text{Cl}$   $\Pi_1$ -(88)  
 $\Pi_2$ -(191)

B.P.	F.P.			
144.5-144.9° at 754.2 mm.	(1)	-26° (13)	$D_4^{20} = 1.1561$ (11)	$n_D^{20} = 1.42162$ (8)
143.8-144.2°	(2)		1.1520 (8)	1.4205 (14)
143.7-144.2° cor.	(3)		1.1498 (14)	1.4203 (11)
143.6° at 760 mm.	(4)			
143.5° at 758 mm.	(5)		$D_{25}^{20} = 1.1573$ (3)	
143° at 756 mm.	(6)			
142.8°	(7)			
142.6-143.0° at 750 mm.	(8)			
142.0-142.3° at 743 mm.	(9)			
141-142.5° at 738 mm.	(10)			
140-142° at 735 mm.	(11)			
52° at 20 mm.	(12)			

Colorless liq.; for constant-boilg. mixt. of  $\bar{C}$  with various org. epds. see Beil. II<sub>2</sub>-(191) or (4) (15) (16) — [For insecticidal actn. see (17); for use in refining of mineral oil see (18).]

[For prepn. of  $\bar{C}$  from chloroacetic acid (3:1370) with EtOH + dry HCl gas (10) cf. (72.5% yield (22)) or  $\text{H}_2\text{SO}_4$  (70% yield (23)) (19) or anhydrous  $\text{MgCl}_2$  (20) see indic. refs.; from chloroacetyl chloride (3:5235) with EtOH (5) or with triethyl orthoformate (1:3241) at 100-110° (90% yield (21)) see indic. refs.; from  $\alpha,\beta$ -dichlorovinyl ethyl ether (3:5540) with org. acids see (24) (25).]

[For formn. of  $\bar{C}$  from ethyl hydroxyacetate (ethyl glycolate) with  $\text{PCl}_5$  see (26); from ethyl aminoacetate hydrochloride with  $\text{NaNO}_2$  + excess HCl see (27); from ethyl diazoacetate with HCl (27) (28) or with  $\text{HgCl}_2$  (70% yield (11)) see indic. refs.; from dichloroacetaldehyde monoethyl hemiacetal (3:5310) with alc. KCN at 20° (38% yield) see (29); from ethyl  $\alpha$ -chloroacetoacetate (3:6207) with diethyl sodiomalonate see (30).]

$\bar{C}$  refluxed with KF yields KCl + ethyl hydroxyacetate (+ some ethyl fluoroacetate) (31);  $\bar{C}$  with  $\text{MgI}_2$  in ether (32) or KI in alc. (3) (34) or in acetone at ord. temp. (35) yields ethyl iodoacetate, b.p. 180°. [For studies on rate of reactn. of  $\bar{C}$  with KI in acetone see (36) (37) (38); with NaI or LiI in acetone see (38).]

[ $\bar{C}$  with Al/Hg + a trace of alc. (39) or with Mg + trace of  $\text{I}_2$  in ether (40) or  $\bar{C}$  with Mg + trace  $\text{HgCl}_2$  in ether (41) yields ethyl  $\gamma$ -chloroacetoacetate (3:6375), b.p. 205°;  $\bar{C}$  with NaCN (25) or KCN (42) yields ethyl cyanoacetate,  $\bar{C}$  with ethyl sodioacetoacetate gives (56-62% yield (23)) diethyl acetosuccinate.]

[ $\bar{C}$  with 2 moles  $\text{MeMgBr}$  (but not  $\text{MeMgI}$ ) in ether gives (yield: 60% (43), 38% (44)) 1-chloro-2-methylpropanol-2 (3:7752) (note, however, that  $\bar{C}$  with a large excess  $\text{MeMgBr}$  (4 moles) gives (40% yield (45)) 2-methylbutanol-3 (1:6170) (3,5-dinitrobenzoate, m.p. 74-75°): for reactn. of  $\bar{C}$  with  $\text{EtMgBr}$  yielding (46) 3-(chloromethyl)-pentanol-3 [Beil. 1-412], with isopropyl  $\text{MgCl}$  (47), or with phenyl  $\text{MgBr}$  (3 moles) yielding (48) chloromethyl-diphenyl-carbinol [Beil. VI-685] see indic. refs.]

[For use of  $\bar{C}$  with Zn (or Zn + Cu (49)) + ketones to give by Reformatsky reactn. (50)  $\beta$ -hydroxy-esters see indic. refs.]

$\bar{C}$  treated with aq. benzenediazonium chloride + NaOAc gives (15% yield (6)) ethyl  $\gamma$ -chloro- $\beta$ -phenylhydrazono-acetoacetate, m.p. 92-93° (6).

$\bar{C}$  with  $\text{Me}_2\text{N}$  in alc. followed by treatment with 100% hydrazine hydrate as directed (51) (52) gives 83-89% yield (51) betaine hydrazide hydrochloride,  $(\text{CH}_3)_2\text{N}(\text{Cl}).\text{CH}_2$ -

CO.NH.NH<sub>2</sub> (Girard's reagent for ketones), m.p. 102°. [For corresp. reactn. using pyridine instead of Me<sub>2</sub>N see (52).]

$\bar{C}$  shaken in cold with 2 vols. conc. aq. NH<sub>4</sub>OH gives (53) (54) (28) (29) (78-84% yield (55)) chloroacetamide, cryst. from aq., m.p. 110-120° (55), 120° (28). —  $\bar{C}$  htd. at 100° for ½ hr. with 2 moles aniline, cooled, aniline hydrochloride extracted with aq. gives (100% yield (56)) (57) (58) ethyl anilinoacetate (phenylglycine ethyl ester) [Beil. XII-470, XII-(263)], cryst. from dil. alc. (56) (57) or lgr. (58), m.p. 58° (58), 57-58° (57), 57° (56). [This prod. on boilg. with excess aniline yields (57) anilinoacetanilide (phenylglycine anilide) [Beil. XII-556], m.p. 110-111° (57).] —  $\bar{C}$  ltd. with aq. benzylamine yields (59) chloroacet-N-benzylamide, m.p. 93.0-93.6° cor. (59).

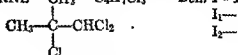
[ $\bar{C}$  with ethyl carbamate ("urethane") + Na in dry ether as directed gives (51-57% yield (60)) triethyl N-tricarboxylate = N(COOC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> [Beil. III-28], b.p. 146-147° at 12 mm. (60).]

$\bar{C}$  htd. as directed (60) with K tetrachlorophthalimide yields N-(carbethoxymethyl)-tetrachlorophthalimide, ndls. from CHCl<sub>3</sub> on pouring into 2 vols. MeOH, m.p. 180-181° (60);  $\bar{C}$  with Na phthalimide yields (61) N-(carbethoxymethyl)phthalimide, m.p. 112-113° (61);  $\bar{C}$  with K 3-nitrophthalimide yields (62) N-(carbethoxymethyl)-3-nitrophthalimide, ndls. from alc., m.p. 70-80° (62).

$\bar{C}$  on hydrolysis (e.g., by boilg. 10 min. with N/10 aq. Ba(OH)<sub>2</sub> (14)) yields ethyl alcohol (1:6130) and chloroacetic acid (3:1370). [For studies on the kinetics of hydrolysis of  $\bar{C}$  under various conditions see Beil. II-2-(191-192) and (2) (14) (63) (64) (65).]

(54) Tröger, Hille, *J. prakt. Chem.* (2) 71, 204 Note (1905). (55) Jacobs, Heidelberg, *Org. Syntheses*, Coll. Vol. 1 (2nd ed.), 153-154 (1941); (1st ed.), 147-148 (1932); 7, 16-17 (1927). (56) Gault, *Bull. soc. chim.* (4) 3, 370 (1908). (57) Meyer, *Ber.* 8, 1156-1158 (1875). (58) Bischoff, Hausdorfer, *Ber.* 25, 2270 (1892). (59) Buehler, Mackenzie, *J. Am. Chem. Soc.* 59, 421-422 (1937). (60) Allen, Nicholls, *J. Am. Chem. Soc.* 56, 1409-1410 (1934). (61) Weisz, Lanyi, *Magyar Chem. Folyóirat*, 39, 153-155 (1933); *Cent.* 1934, I 2746, *C.A.* 28, 5815 (1934). (62) Sah, Ma, *Ber.* 65, 1630-1633 (1932). (63) Sapazhnikova, *J. Phys. Chem. (U.S.S.R.)* 13, 174-185 (1939), *C.A.* 34, 311 (1940). (64) Anantakrishnan, Krishnamurti, *Proc. Indian Acad. Sci.* 14-A, 270-278, 279-283 (1941), *C.A.* 36, 1837 (1942). (65) Newling, Hinshelwood, *J. Chem. Soc.* 1936, 1357-1361. (66) Allen, Bell, *Org. Syntheses*, 24, 60-61 (1944).

3:5710 1,1,2-TRICHLORO-2-METHYLPROPANE  $\text{CH}_3 \quad \text{CH}_2 \quad \text{C}_4\text{H}_7\text{Cl}_3$  Beil. I - 126



B.P. M.P.  
144.5-145.4° cor. (1) -6.5 to -6.0° (1)  $D_4^{25} = 1.2712$  (1)  
145-146° at 762 mm. (2)  $n_D^{20} = 1.4666$  (1)  
46-47° at 18 mm. (2)

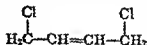
[For prepn. (together with other products) from *ter*-butyl chloride (3:7045) +  $\text{Cl}_2$  see (1), for formn. (32%) (together with 68% 3,3-dichloro-2-methylpropene-1) from 1-chloro-2-methylpropene-1 (3:7120) with  $\text{Cl}_2$  +  $\text{NaHCO}_3$  at 0° see (2).] [The product described in Beil. I-126 was very impure (1).]

$\bar{\text{C}}$  on further chlorination yields (1) 1,1,1,2-tetrachloro-2-methylpropane (3:4725), m.p. 179°.

$\bar{\text{C}}$  on prolonged refluxing with dil.  $\text{NaOH}$  loses  $\frac{1}{2}$  of its chlorine (1) but the reactn. products were not characterized.

3:5710 (1) Rogers, Nelson, *J. Am. Chem. Soc.* 58, 1027-1029 (1936). (2) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232-1246 (1938), *C.A.* 33, 4190 (1939); *Cent.* 1939, II 4222.

3:5725 1,4-DICHLOROBUTENE-2  $\text{Cl} \quad \text{Cl} \quad \text{C}_4\text{H}_6\text{Cl}_2$  Beil. S.N. 12



B.P. 145° (1)  $n_D^{30} = 1.4745$  (1)  
75-70° at 40 mm. (1)

For this structure two geom. stereoisomers are theoretically possible but only  $\bar{\text{C}}$  (configuration undetermined) is known.

[For prepn. of  $\bar{\text{C}}$  together with other products) from butadiene-1,3 with  $\text{Cl}_2$ , either directly or in  $\text{CHCl}_3$ ,  $\text{CS}_2$ , or lgr. soln. see (1) (2); the process can be controlled so as to yield little or no 1,2,3,4-tetrachlorobutane but rather a mixt. of  $\bar{\text{C}}$  and 1,2-dichlorobutene-3 (3:5350) in the ratio 1:2 (1) (2); for prepn. of  $\bar{\text{C}}$  from 1,2-dichlorobutene-3 (3:5350) via allylic transposition in pres. of metal halide cat (3) such as  $\text{AlCl}_3$  (4) see (3) (4).]

$\bar{\text{C}}$  does not (1) rearr. to 1,2-dichlorobutene-3 (3:5350) even on htg. at 90° in a s.t.

$\bar{\text{C}}$  on htg. at 90° with 2 pts. solid  $\text{KOH}$  loses  $\text{HCl}$  yielding (1) 1-chlorobutadiene-1,3 (3:7210), b.p. 85° (1).

$\bar{\text{C}}$  on htg. in alc. with  $\text{Zn}$  dust yields (1) butadiene-1,3.

$\bar{\text{C}}$  with  $\text{Cl}_2$  yields mainly (1) the solid form (m.p. 72°) of 1,2,3,4-tetrachlorobutane (3:1760).

$\bar{\text{C}}$  on oxidn. with dil. alc.  $\text{KMnO}_4$  or with  $\text{O}_3$  followed by aq. gives (1) chloroacetic acid (3:1370).

3:5725 (1) Muskat, Northrup, *J. Am. Chem. Soc.* 52, 4043-4055 (1930). (2) Muskat (to du  
 {3} I. G. Farben-  
 (1939); Nicodemus,  
 Nicodemus (to I.G.),

3:5735  $\beta$ -CHLOROETHYL ACETATE

Beil. II - 128

 $\Pi_1$ -(57) $\Pi_2$ -(136)

B.P. 145° (1)

 $D_{25}^{27} = 1.1455$  (2)  $n_D^{20} = 1.4234$  (2) (3)

142-144° at 743 mm. (2)

142.4-143.8° at 733 mm. (3)

Colorless oil, insol. aq.

[For prepn. from  $\beta$ -chloroethanol (3:5552) by actn. of  $AcCl$  (90% yield (4), 82% yield (5)) see (4) (5) (6); by actn. of  $Ac_2O$  at 116° see (7); for prepn. from ethylene oxide (1:6105) +  $AcCl$  see (3) (8); for prepn. from ethylene glycol diacetate (1:3511) +  $HCl$  + ht. + pressure see (9); for prepn. from ethylene +  $Cl_2$  +  $Ac_2O$  see (2) (10); for prepn. (95.5% yield (11)) from di-( $\beta$ -chloroethyl) sulfate +  $NaOAc$  +  $AcOH$  see (11); for still other misc. methods see Beil. II-128.]

[For study of reactivity toward  $KI$  in acetone at 50° and 60° see (12); for study of pyrolysis (to vinyl chloride) see (13); for conversion to ethylene oxide (1:6105) by treatment with alk. see (14) (15).]

$\bar{C}$  htd. at 100° for 5 hrs. with thiourea (1 mole) gives 100% yield of  $S$ -( $\beta$ -acetoxyethyl)-isothioureas hydrochloride, cryst. from mixt. of alc. + acetone, m.p. 136-137° (17).

$\bar{C}$  on hydrolysis yields  $\beta$ -chloroethanol (3:5552) +  $AcOH$ . [For study of hydrolysis by  $N/10 HCl$  see (16).]

⑧  $N$ -( $\beta$ -Acetoxyethyl)tetrachlorophthalimide: pl. from  $CHCl_3$  poured into 2 vols.  $MeOH$ , m.p. 168-169° (18). [From  $\bar{C}$  +  $K$  tetrachlorophthalimide (18).]

3:5735 (1) Simpson, *Ann.* 112, 149 (1859). (2) Baum, Vogt, Hennion, *J. Am. Chem. Soc.* 61, 1458 (1939). (3) Gustus, Stevens, *J. Am. Chem. Soc.* 55, 383 (1933). (4) Bogert, Sloeum, *J. Am. Chem. Soc.* 46, 766 (1924). (5) Blicke, Blake, *J. Am. Chem. Soc.* 53, 1018 (1931). (6) (8) Altwegg, Landriven, man (to Dow Chem. Co.), 720, Feb. 3, 1937; C.A. 31,

4015 (1937).

(11) Suter, Evans, *J. Am. Chem. Soc.* 60, 537 (1938). (12) Conant, Kirner, Hussey, *J. Am. Chem. Soc.* 47, 498 (1925). (13) Büger, Hibbert, *J. Am. Chem. Soc.* 58, 825 (1936). (14) Britton, Coleman, Mate (to Dow Chem. Co.), U.S. 2,022,182, Nov. 20, 1935; C.A. 30, 737 (1936); Cent. 1936, 1, 2025. (15) 117. (17) 371-2. (18) 1.

3:5745 2,2-DICHLOROETHANOL-1  
 ( $\beta,\beta$ -Dichloroethyl alcohol)

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 $I_1$ — $I_2$ —

B.P. 140° (1)

 $D_{15}^{19} = 1.416$  (2) $n_D^{17.3} = 1.4752$  (2)

140-146° (2)

Colorless liq.; sparingly sol. aq., sol. alc. or ether; volatile with steam.

[For prepn. of  $\bar{C}$  from  $\beta,\beta$ -dichloroacetaldehyde (3:5180) with  $Al(OEt)_3$  in abs. alc. (2) or with diethylzinc followed by aq. (1) see indic. refs.]

$\bar{C}$  reduces  $NH_4OH/AgNO_3$  (1) (2).

$\bar{C}$  on oxidn. with  $HNO_3$  yields (1) dichloroacetic acid (3:6208).

3:5745 (1) Delacre, *Jahresber.* 1887, 1247. (2) Boeseken, Tellegen, Plusje, *Rec. trav. chim.* 57, 75-76 (1938)

3:5750 1,1,2,2-TETRACHLOROETHANE  $Cl_2CH-CHCl_2$   $C_2H_2Cl_4$  Beil. I - 86  
(Acetylene tetrachloride;  
sym.-tetrachloroethane)  $I_1$ -(25)  
 $I_2$ -(55)

B.P.	F.P.			
147° cor.	(1) -44° (17)	$D_4^{25} = 1.5881$ (12)		
146.2-146.8°	-43.8° (4)	1.5869 (19)		
at 760 mm. (2)	(5)	(20)		
146.35°	(3) -43.5° (18)	1.58658 (5)		
146.3° at 758 mm. (17)	-42.5° (6)		$n_D^{24} = 1.501$ (21)	
146.25° (4)	(18)			
146.2-146.7° cor.		$D_4^{20} = 1.5966$ (2)	$n_D^{20} = 1.49509$ (22)	
at 756 mm. (20)		1.59457 (5)	1.4947 (13)	
146.20° at 760 mm. (5) (6)		1.5943 (9)	1.49419 (8)	
145.6° (7)			1.49415 (2)	
145.2° at 748 mm. (8)			1.4040 (9)	
145.2° at 737 mm. (9)				
145-146° at 753 mm. (10)			$n_D^{15.6} = 1.49490$ (23)	
145.0° (11)				
144.7° at 751 mm. (12)			$n_D^{17} = 1.49559$ (24)	
144.5° (13)				
144.0-144.8° (14)		$D_4^{15} = 1.60255$ (5)	$n_D^{15} = 1.49678$ (5)	
143.5-144° (15)		1.6015 (12)		
140.6° at 675 mm. (12)				
136.0° at 594 mm. (12)		For $D_4^i$ from -21°	For $n_D^i$ from 13-25°	
130.0° at 502 mm. (12)		to 128° see (17).	see (11).	
125.3° at 435 mm. (12)				
120.5° at 372 mm. (12)				
115.0° at 313 mm. (12)				
108.0° at 252 mm. (12)				
102.0° at 203 mm. (12)				
99.0° at 132 mm. (12)				
80.0° at 89 mm. (12)				
62.0° at 45 mm. (12)				
55.5-56.3° at 31 mm. (16)				
55° at 17 mm. (12)				

Note: Care must be taken not to confuse  $\bar{C}$  with tetrachloroethylene (3:5460) or with 1,1,1,2-tetrachloroethane (unsym.-acetylene tetrachloride (3:5555)).

Colorless liq. with odor similar to that of chloroform. — [For vapor press. of  $\bar{C}$  at intervals over range 20-145° see (25); for study of thermal conductivity see (26).]

$\bar{C}$  is very spar. sol. aq.: e.g., 100 g.  $H_2O$  at 20° dis. 0.283 g.  $\bar{C}$ ; at 55-56° dis. 0.336 g.  $\bar{C}$  (27); 1 g.  $\bar{C}$  is sol. at 25° in 350 g. aq. (101); for soly. of  $H_2O$  in  $\bar{C}$  at 0°, 25°, and 30° as

detd. by Karl Fischer reagent. see (28). —  $\bar{C}$  is easily volatile with steam (for use in detn. of  $H_2O$  see below).

### MISCELLANEOUS PHYSICAL PROPERTIES

[For soly. in  $\bar{C}$  of dry gaseous  $HCl$  (14) (15),  $H_2S$  (14), or  $O_2$  (29) see indic. refs.; for soly. in  $\bar{C}$  at 11–25° of  $I_2$  (30) and use of such solns. in detn. of iodine number (31) see indic. refs.; for adsorption by activated carbon of  $I_2$  from solns. in  $\bar{C}$  see (32).]

[For study of influence of vapors of  $\bar{C}$  on the explosion limits of mixtures of air with hydrogen (33), acetylene (33), methane (33) (34) (35), or carbon monoxide (33) (36) see indic. refs.]

[For prepn. of and comparison with  $\bar{C}$  of *sym.*-dideuterio-1,1,2,2-tetrachloroethane,  $Cl_2C(D)_2$ , see (9).]

Binary systems contg.  $\bar{C}$ . [For f.p./compn. data and/or diagrams on systems  $\bar{C}$  + 1,2-dichloroethane (ethylene dichloride) (3:5130) (18);  $\bar{C}$  + 1,1,2-trichloroethane (3:5330) (18);  $\bar{C}$  + pentachloroethane (3:5880), eutectic, f.p. –73°, contg. 40.1%  $\bar{C}$  (18);  $\bar{C}$  + *cis*-dichloroethylene (3:5042) (37);  $\bar{C}$  + *trans*-dichloroethylene (3:5028) (37);  $\bar{C}$  + *p*-dichlorobenzene (3:0980) (38);  $\bar{C}$  + 1,2-dibromoethane (ethylene dibromide) (18);  $\bar{C}$  + 1,1,2,2-tetrabromoethane (acetylene tetrabromide) (18);  $\bar{C}$  + succinonitrile (18); or  $\bar{C}$  + succinic acid (1:0530) (18) see indic. refs. — For study of system  $\bar{C}$  + naphthalene (1:7200) at 30° under press. up to 1000 atm. see (39).]

$\bar{C}$  with various org. cpds. forms binary azeotropes [e.g.,  $\bar{C}$  with anhydrous formic acid (1:1005) forms a const.-boilg. mixt., h.p. 99.25° at 760 mm., contg. 32 wt. %  $\bar{C}$  (40); note that  $\bar{C}$  with  $AcOH$  (1:1010) does *not* form a const.-boilg. mixt. (41) (the data listed by "Int. Crit. Tables" for such an azeotrope is actually for the mixt.  $AcOH$  + tetrachloroethylene);  $\bar{C}$  with propionic acid (1:1025) forms a const.-boilg. mixt., b.p. 140.4° at 760 mm., contg. abt. 40 wt. %  $\bar{C}$  (42); for other azeotropes see Beil. II<sub>2</sub> (56). — Note that no record of formn. of azeotropes of  $\bar{C}$  with  $MeOH$  or  $EtOH$  can be found.]

Ternary systems contg.  $\bar{C}$ . [For soly. data and diagrams of system  $\bar{C}$  + acetone (1:5400) + aq. see (43).]

### USES OF $\bar{C}$

$\bar{C}$  is widely used in industry as a solvent and as an intermediate in the manufacture of various other chlorinated solvents, notably trichloroethylene (3:5170); for additional examples of special uses see also below.

$\bar{C}$  is frequently employed as solvent in certain types of Friedel-Crafts reactions or phthalic anhydride condensations [for study of use of  $\bar{C}$  as solvent in Friedel-Crafts condensation of phenol with high-mol.-wt. acyl chlorides see (44)].

[For use of  $\bar{C}$  as swelling agent for rubber (45), in prod. of films from rubber hydrochloride (46), in prod. of cellulose acetate by pptn. from  $\bar{C}$  with hydrocarbons (47) (note that acetylcelluloses give with  $\bar{C}$  crystalline addition prods. (48)), together with aliphatic monohydric alcs. as solv. for cellulose alkyl ethers (49), in prepn. of transparent cellulose acetate plastics (50) see indic. refs. — For soly. of various polymers in  $\bar{C}$  see (56).]

[For use of  $\bar{C}$  as catalyst in condensation of phenol with formaldehyde (51) or furfural (52) see indic. refs.]

[For use of  $\bar{C}$  with petroleum naphtha as a dry-cleaning fluid (53), for use of  $\bar{C}$  as a rust remover (54), as means of removing mud barriers in oil wells (55), or as an immersion fluid in opt. crystallog. (21) see indic. refs.]

[For use of  $\bar{C}$  (57) (58) or stable aq. emulsions of  $\bar{C}$  (59) as weed killers see indic. refs.]

[For studies of use of  $\bar{C}$  in detn. of theobromine in cacao see (60) (61) (62) (63).]

[For use of  $\bar{C}$  as anti-moth prod. (64), as a component of insecticides (65), together with

$\text{CS}_2$  and chlorobenzene (3:7903) as insecticide (66), or together with 20% trichloroethylene (3:5170) as a fumigant and insecticide (67) see indic. refs.]

[For studies on antiseptic, bactericidal, and disinfectant action of  $\bar{\text{C}}$  see (68) (69) (70).]

$\bar{\text{C}}$  is also employed for the detn. of  $\text{H}_2\text{O}$  by distillation; note that besides being non-inflammable  $\bar{\text{C}}$  is also much denser than water which for some applications of this method is advantageous. — [For general discussion and examples of this procedure see (226) (70) (71) (72) (73) (74) (75); for comparison of results with those obt'd. by oven drying see (76); for application to detn. of  $\text{H}_2\text{O}$  in liquid and solid fuels (77) (78), in glycerol (79) (80), in liquid glue (81), in cereal (82), in dried apples (83), in cooking salt (84) see indic. refs.]

### TOXICITY AND PHYSIOLOGICAL ACTION OF $\bar{\text{C}}$

$\bar{\text{C}}$  is the most toxic of the group of chlorinated hydrocarbons (85) and produces marked pathological alterations in gastrointestinal tract, liver, and kidneys. — [Detailed discussion of this aspect of  $\bar{\text{C}}$  is beyond the scope of this treatment except to cite references (229) (227) (232) and (85)–(99), incl. (note that articles on this topic prior to 1930 are omitted).]

[For discussion of fate of  $\bar{\text{C}}$  in body see (100). — Note also that  $\bar{\text{C}}$  (in sharp contrast to the closely related tetrachloroethylene (3:5460)) has no efficacy as anthelmintic for hookworms (101).]

[For actn. of  $\bar{\text{C}}$  on alc. fermentation see (102) (103); for actn. on invertase see (104).]

### DETERMINATION OF $\bar{\text{C}}$

Some methods for the deto. of  $\bar{\text{C}}$  involve conversion of all of its halogen to chloride ion and subsequent volumetric or gravimetric detn. of the latter; e.g., for methods based on initial pyrolytic decomposition see (105) (89) (106) (107); for methods based on debalogenation of  $\bar{\text{C}}$  with Na + ethanolamine in dioxane see (108) (230) (note that use of Na in liq.  $\text{NH}_3$  causes some cyanide formn. (109)). — For detn. of  $\bar{\text{C}}$  by means of elimination of 1 HCl with cold alc. KOH see (110). — For detn. of  $\bar{\text{C}}$  by means of the Fujiwara color reactn. with NaOH/pyridine see (111). — Note that  $\bar{\text{C}}$  does not respond to the R + H "Tri-Per-Analyzer" (a recording ultra-violet photometer) (112). — For further comments on detection of  $\bar{\text{C}}$  see below under color tests.

### PREPARATION OF $\bar{\text{C}}$

$\bar{\text{C}}$  is one of a large family of "chlorinated solvents" now available from industrial sources. — The most-studied method of prepn. is that from acetylene by controlled addition of chlorine, although variants of this method are employed and other starting prods. (see below) are sometimes used. —  $\bar{\text{C}}$  is also obtained as a by-prod. of the manufacture of the comml. mixt. (3:5030) of the two stereoisomeric 1,2-dichloroethylenes, *cis* (3:5042) and *trans* (3:5025), 1,1,2-trichloroethane (3:5330), etc.

From acetylene by addition of chlorine. Under suitable controls to avoid explosion and with the assistance of a wide variety of catalysts  $\bar{\text{C}}$  is manufactured from acetylene by reaction with  $\text{Cl}_2$ . — [For a concise review of the general nature and difficulties of this general method see (113).]

[For important general articles on this synthesis see (114)–(122) incl. — For examples of patents employing this method see refs. (123)–(138) incl.; for special test of Cer. 204,833 (131) see (118) (120); for test of Cer. 154,677 (133) see (119) (120).]

From acetylene by other means. [For prepn. of  $\bar{\text{C}}$  from acetylene with excess  $\text{SbCl}_5$  (139) (234) with  $\text{SbCl}_3 + \text{SbCl}_5$  (140), with  $\text{NOCl}$  (4 moles) at  $350^\circ$  (141), with aq.  $\text{NaOCl}$  soln. (142), with  $\text{S}_2\text{Cl}_2 + \text{Fe}$  powder in cold (143) (144) see indic. refs.]



From ethylene. [For formn. of  $\bar{C}$  from ethylene +  $Cl_2$  (as hy-prod. of prepn. of ethylene chlorohydrin (3:5552)) (145), from ethylene +  $Cl_2$  (as hy-product of prepn. of 1,1,2-trichloroethane (3:5330)) (146) (147), from ethylene +  $Cl_2$  (as hy-prod. of a three-part process for combined prepn. of  $\bar{C}$  + ethyl chloride) (198) see indic. refs.]

From dichloroethylenes. [For prepn. of  $\bar{C}$  from *cis*-dichloroethylene (3:5042) in vapor phase at 95° in light of 4360 Å with  $Cl_2$  (in absence of  $O_2$ ) (149), or in liq. phase with  $SO_2Cl_2$  (1½ moles) in pres. of trace of dibenzoyl peroxide refluxed 3 hrs. in dark (85% yield (150)), see indic. refs.]

[For prepn. of  $\bar{C}$  from *trans*-dichloroethylene (3:5028) in vapor phase at 80–95° in light of 4358 Å with  $Cl_2$  see (151).]

[For prepn. of  $\bar{C}$  from ord. mixt. (3:5030) of both stereoisomeric dichloroethylenes with  $Cl_2$  (13) in light of 4360 Å (152) see indic. refs.]

From trichloroethylene. [For formn. of  $\bar{C}$  (together with other prods.) from trichloroethylene (3:5170) +  $AlCl_3$  +  $HCl$  gas at 50° see (153).]

From 1,2-dichloroethane (ethylene (di)chloride). [For prepn. of  $\bar{C}$  from ethylene (di)chloride (3:5130) with  $Cl_2$  (148) in u.v. light see (154).]

From miscellaneous starting points. [For formn. of  $\bar{C}$  usually together with other prods. from dichloroacetaldehyde (3:5180) with  $PCl_5$  (1), from "β-chlorovinyl iodochloride" ( $ClCH=CH.ICl_2$ ) on warming (15), from 1,1,2-trichloro-2-iodoethane on distn. at ord. press. (155), from 1,2-di-iodoethylene with  $Cl_2$  (156), or from 1,1,2-trichloroethane (3:5330) with  $Cl_2$  +  $AlCl_3$  at 70–80° (231) see indic. refs.]

### STABILIZATION OF $\bar{C}$

[For patents on stabilization of  $\bar{C}$  by addition of small amts. of phenols, aminophenols, etc. (157), or by addn. of less than 0.1% alkylamines (158) see indic. refs.]

### CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis without catalyst.  $\bar{C}$  on protracted reflux (20 days (159)) or techn.  $\bar{C}$  on repeated distn. (160) leaves a residual high-boilg. fraction ("Tetranachlauf") consisting mainly of 1,1,2,3,4,4-hexachlorobutane (3:3155), ndls. from alc., m.p. 107° (159) (160), presumably formed by elimination of 1 Cl atom from each of 2 moles of  $\bar{C}$ . — [ $\bar{C}$  htd. in s.t. at 300° for 15 hrs. yields (139) trichloroethylene (3:5170);  $\bar{C}$  in s.t. at 360° for 100 hrs. yields (139) hexachlorobenzene (3:4939).]

Pyrolysis in pres. of various catalysts or  $HCl$  acceptors.  $\bar{C}$  on suitable hgt. particularly in the pres. of dehydrohalogenating catalysts or acceptors of the hydrogen chloride formed loses 1 mole  $HCl$  yielding trichloroethylene (3:5170). (For elimination of  $HCl$  by chemical means such as alk.,  $NH_3$ , etc., see below.)

[E.g.,  $\bar{C}$  over pumice at 700° (161), over pumice contg.  $Cu_2(PO_4)_3$  at 450–500° (162), over  $ThO_2$  below 390° (163) cf. (164), over  $BaCl_2$  at 300° (165), over bone char at 300–310° (166), over activated carbon at 200–300° (167), 260° (168) (note yield diminishes with increasing temp. (233)) or 500° (169), or over suitable cat. (148) loses  $HCl$  yielding trichloroethylene (3:5170). — Note also that pure  $\bar{C}$  on long exposure to u.v. light loses  $HCl$  bimolecularly yielding (159) 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), m.p. 80°.]

[ $\bar{C}$  + acetylene over cat. at 250° loses  $HCl$  yielding (167) trichloroethylene (3:5170) + vinyl chloride (3:7010);  $\bar{C}$  with  $MeOH$  over  $Al_2O_3$  at 280° loses  $HCl$  yielding (170) trichloroethylene (3:5170) + methyl chloride (3:7005).]

Dehydrogenation. [ $\bar{C}$  with air over pumice contg.  $CuCl_2$  at 430–450° (171), or with  $Cl_2$  over activated carbon contg.  $CuCl_2$  at 300–320° (172), or with hexachloroethane (3:4835) over cat. at 200–400° (173) loses its two hydrogenations yielding tetrachloroethylene (3:5460).]

(Partial) dehalogenation.  $\bar{C}$  with  $H_2$  over Ni at 300–320° (174), or  $\bar{C}$  with Fe or Al + aq. (175) (176) or Zn + aq. (176) (177), or  $\bar{C}$  with acetylene over hydrogenating cat. (such as Ni) on activated carbon at 350° (178) preferably in pres. of aq. vapor (179) or on electrolytic reductn. in pres. of  $ZnCl_2$  (235) (236) loses 1 chlorine from each carbon atom yielding a mixt. (3:5030) of the two stereoisomeric 1,2-dichloroethylenes. — Note that  $\bar{C}$  with Zn in alc. yields (180) acetylene.]

Oxidation.  $\bar{C}$  with air in ultra-violet light yields (181) (182) dichloroacetyl chloride (3:5290) (or in pres. of aq. dichloroacetic acid (3:6208)), accompanied by small amts. of oxalic acid and an octachlorobutane, m.p. 81°. (Note also that pure  $\bar{C}$  on long exposure to u.v. light loses HCl bimolecularly yielding (159) 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), m.p. 80°.)]

[For behavior of  $\bar{C}$  with  $CrO_3/H_2SO_4$  (183) or over hot CuO (184) see indic. refs.]

#### BEHAVIOR WITH HALOGENS

Fluorination.  $\bar{C}$  with  $F_2$  gas at 50° for 14 hrs. gives (185) 1-fluoro-1,1,2,2-tetrachloroethane, b.p. 115.5–116.5°,  $D_4^{20} = 1.6218$ ,  $n_D^{20} = 1.4487$ , and 1,2-difluoro-1,1,2,2-tetrachloroethane, b.p. 92–93°, m.p. 24–25°, together with various other prods. — For fluorination of  $\bar{C}$  with  $SbF_3 + SbCl_5$  see (186)].

Chlorination.  $\bar{C}$  with  $Cl_2$  (139) in  $CCl_4$  sola. (187), in u.v. light (188) or X-radiation (189), or over activated carbon at 300–400° (190) (191), or in liq. phase at 60–70° (192), or with Fe at 20–80° (192), or with  $AlCl_3$  at 20–100° (192), or under reflux at 120° (80% yield (193)), or  $\bar{C}$  with anhydr.  $FeCl_3$  on hgt. in s.t. (194), or even  $\bar{C}$  with aq. bleaching powder (192) yields hexachloroethane (3:4835).]

#### BEHAVIOR WITH $H_2SO_4$

$\bar{C}$  with fuming  $H_2SO_4$  (65%  $SO_3$ ) in pres. of  $HgSO_4$  at 50–60° readily gives (198) (yields: 70–73% (195), 32% (196), 30% (197)) glyoxal sulfate,  $O_2SO_2CH-CHO_2SO_2$ , [Berl. 17- (818)], adls. from  $ClSO_3H$ , m.p. 176–177° (198), ndls. with 1 AcOH, m.p. 121–122° from AcOH, the solv. of crystn. being lost completely in vac. over NaOH (199).

#### BEHAVIOR WITH ALKALINE REACTANTS

$\bar{C}$  under influence of many alk. reactants loses 1 mole HCl; this reactn. is used for the manufacture of trichloroethylene (3:5170) (see also above under pyrolysis of  $\bar{C}$ ) and also by titration of the HCl or estimation of chloride ion formed as a diagnostic test for  $\bar{C}$  (see below)

$\bar{C}$  on hgt. with aq. alk. or alk. carbonates (200) in pres. of tetraethylene glycol as promoter (228) or with aq.  $Ca(OH)_2$  or alk. carbonates (200) (201) (234) (114) (for test of Ger. 171,900 (200) see (202) (120)), or  $\bar{C}$  with alc. KOH (203) cf. (122) or alc. NaOEt (203), loses 1 mole HCl yielding trichloroethylene (3:5170); note that in use of alc. alkali, distn. gives the const.-boil. mixt. of EtOH with trichloroethylene, b.p. 70–71°, from which latter is separated by washing with aq. and subsequent drying over  $CaCl_2$  (203).

$\bar{C}$  with EtOH/NaOH or EtOH/NaOEt (204) cf. (205), or  $\bar{C}$  with 1 N EtOH/KOH in xylene (110), instantly and quant. splits out 1 HCl at room temp.; note that this does not occur with *cis*-dichloroethylene (3:5042), *trans*-dichloroethylene (3:5028), trichloroethylene (3:5170) or tetrachloroethylene (3:5460), chloroform (3:5050), or carbon tetrachloride (3:5100), but does occur in analogous fashion with pentachloroethane (3:5880) (110). — [For rate of reactn. of  $\bar{C}$  with KOH in 95% EtOH at 90° see (206).]

Note, however, that  $\bar{C}$  in acetone with excess standard alk. refluxed 3 hrs., then residual alk. titrated back, uses 5 equivalents of alk. (207); this surprising result is presumably to

be attributed to hydrolysis of  $\bar{C}$  to glyoxal followed by disproportionation of latter to sodium glycolate; cf. (208).

$\bar{C}$  with solid KOH on htg. yields (203) dichloroethylene (3:5030), trichloroethylene (3:5170), tetrachloroethylene (3:5460), together with a spontaneously inflammable gas which may be chloroacetylene (3:7000). —  $\bar{C}$  with anhyd. KOH in xylene at 80° under  $N_2$  gives (209) a little dichloroacetylene (3:5010) (may be carried out as a lecture experiment (209)).

#### BEHAVIOR OF $\bar{C}$ WITH $NH_3$ AND AMINES

[ $\bar{C}$  with excess  $NH_3$  gas in pres. of aq. (210), or with aq.  $NH_4OH$  htd. under press. (210) (120), or with liq.  $NH_3$  at -40° (211) (212), or with dry pyridine on reflux (182) loses HCl giving (yields: 92% (211) 92-96% (210)) trichloroethylene (3:5170).]

[ $\bar{C}$  htd. with aniline + aq.  $Ca(OH)_2$  at 140-190° under press. yields (213) a mixt. of the calcium salt of *N*-phenylglycine and *N*-phenylglycine anilide, cf. (122); since this reaction really involves conversion of  $\bar{C}$  by loss of HCl to 1,1,2-trichloroethylene (3:5170) and reactn. of latter with aniline see 3:5170 for details.]

$\bar{C}$  with excess phenylhydrazine on stdg. at ord. temp. evolves  $N_2$ , ppts. phenylhydrazine hydrochloride, and yields  $C_6H_6$  (110); the full mechanism of this behavior seems never to have been established, but the same three prods. are also similarly ohtd. from pentachloroethane (3:5880) and hexachloroethane (3:4835).

[For rate of reactn. of  $\bar{C}$  with piperidine in 95% EtOH at 90° see (206).]

#### BEHAVIOR OF $\bar{C}$ WITH METALS

[For survey of action of  $\bar{C}$  on various common metals (214) (215) in pres. of moisture (223) see indio. refs.]

$\bar{C}$  with Na or K or their alloys may (like many other polychloro compounds) explode under certain conditions [for extensive studies of this behavior including sensitivity to mechanical shock see (216) (217)].

#### BEHAVIOR OF $\bar{C}$ WITH METAL SALTS

[ $\bar{C}$  with  $AlCl_3$  at 110° undergoes partial rearr. (218) to the isomeric 1,1,1,2-tetrachloroethane (3:5555). —  $\bar{C}$  with freshly prepared anhyd.  $AlBr_3$  on htg. below h.p. of  $\bar{C}$  yields (219) 1,1,2,2-tetrabromoethane (acetylene tetrahydride) [Beil. I-94, I<sub>1</sub>-(30), I<sub>2</sub>-(66)].]

$\bar{C}$  with *N*/15  $AgNO_3$  in 95% EtOH shows no reactn. even after 12 hrs. at 90° (206) cf. (80).

#### MISCELLANEOUS

[ $\bar{C}$  does not react with excess Hg di-*p*-tolyl (220). —  $\bar{C}$  with excess  $C_6H_5MgBr$  yields 1,1,2,2-tetraphenylethane [Beil. V-739, V<sub>1</sub>-(371), V<sub>2</sub>-(673)] (221) cf. (222).]

#### COLOR REACTIONS OF $\bar{C}$

⊕ With cyclopentanol (1:6412).  $\bar{C}$  (1 drop) with cyclopentanol (2 ml.) + trace solid NaOH, boiled 25 secs., cooled, acidified with AcOH or 85%  $H_2SO_4$ , stood 1 min., shaken gives (224) green color. [Note that this same response is also shown by 1,1,2-trichloroethylene (3:5170) but not by methylene dichloride (3:5020),  $CHCl_3$  (3:5050),  $CCl_4$  (3:5100), ethylene dichloride (3:5130), pentachloroethane (3:5880), *cis*-(3:5042) or *trans*-(3:5028) 1,2-dichloroethylene, or tetrachloroethylene (3:5460); for sensitivity for  $\bar{C}$  see (224).]

With pyridine + NaOH (Fujiwara reagt.) [For detn. of  $\bar{C}$  with Fujiwara reagt. see (111); for relative sensitivity of Fujiwara reagt. to  $\bar{C}$  as compared to  $CHCl_3$  (3:5050),

$\text{CCl}_4$  (3:5100), 1,1,2-trichloroethane (3:5330), trichloroethylene (3:5170), and tetrachloroethylene (3:5460) see [100].]

With  $\text{NH}_4\text{OH}/\text{CuCl}$ . Note that  $\bar{\text{C}}$  with  $\text{NH}_4\text{OH}/\text{CuCl}$  does not give blue color within 5 min. (225) (dif. from pentachloroethane (3:5580) q.v.).

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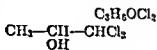
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### 3:5755 1,1-DICHLOROPROPANOL-2

( $\beta$ , $\beta$ -Dichloroisopropyl alcohol;  
dichloromethyl methyl-carbinol)



Beil. I - 363

I<sub>1</sub>—

I<sub>2</sub>-(383)

B.P. 146-148° at 755 mm. (1)

$D_{25}^{25} = 1.3334$  (1)

Moderately sol. aq., very sol. alc., ether.

[For prepn. of  $\bar{C}$  from dichloroacetaldehyde (3:5180) with MeMgBr in dry ether (57.4% yield) see (1); from 1,1-dichloropropanone-2 (unsym.-dichloroacetone) (3:5430) with anhydrous acetaldehyde + Al(OEt)<sub>3</sub> in dry ether (45% yield) see (2).] — [Note that the levorotatory stereoisomer of  $\bar{C}$ , b.p. 146-148°,  $[\alpha]_D^{25} = -0^\circ$ , has been obtd. (54% yield) from unsym.-dichloroacetone (3:5430) by reduction with yeast (3).]


[For behavior of  $\bar{C}$  with NaOEt in alc. or ether see (4).]

[ $\bar{C}$  with paraformaldehyde +  $ZnCl_2$  gives (23.5% yield (5)) formaldehyde bis-( $\beta,\beta$ -dichloroisopropyl)acetal (Beil. I-575), h.p.  $81^\circ$  at 0.2 mm. (4).]

—  $\beta,\beta$ -Dichloroisopropyl benzoate: oil, h.p.  $92-94^\circ$  at 0.15-0.17 mm. (4). [From  $\bar{C}$  with  $BzCl$  refluxed 4 hrs. at  $150^\circ$  (80% yield (4)).]

—  $\beta,\beta$ -Dichloroisopropyl carbamate: unreported. [Note, however, that the corresp. deriv. of levorotatory  $\bar{C}$  (obtd. with carbamyl chloride in ether) has m.p.  $61-63^\circ$  (3).]

3:5755 (1) Wohl, Roth, *Ber.* **40**, 217-218 (1907). (2) Nord, *Ger.* 434,728, Oct. 5, 1926; *Cent.* 1926, II 2845. (3) Sen, *J. Indian Chem. Soc.* **1**, 1-8 (1924/25); *Cent.* 1925, I 537; *C.A.* **19**, 816 (1925); *Biochem. Z.* **151**, 51-53 (1924); *Cent.* 1924, II 2272; *C.A.* **19**, 3277 (1925). (4) Wohl, *Ber.* **41**, 3606-3608 (1908).

3:5760 3,3,3-TRICHLORO-1,2-EPOXYPROPANE  $C_3H_3OCl_3$  Beil. S.N. 2362  
( $\omega,\omega,\omega$ -Trichloropropylene oxide)  $Cl_3C-CH-CH_2$   


B.P. $149^\circ$ at 764 mm. (1)	$D_{44}^{25} = 1.4921$ (4)	$n_D^{25} = 1.4737$ (4)
$149^\circ$ at 750 mm. (2)		
$40^\circ$ at 11 mm. (1)	$D_{44}^{20} = 1.495$ (5)	$n_D^{20} = 1.4768$ (5)
$44-45^\circ$ at 13 mm. (2)		
$41-42^\circ$ at 10 mm. (3)	$D_{44}^{19} = 1.4962$ (5)	
$39-40^\circ$ at 11 mm. (4)		

Colorless mobile liq. with sweetish not unpleasant odor suggesting epichlorohydrin (3:5358). [Note that  $\bar{C}$  was at first (1) erroneously supposed to be 1,1,1-trichloroacetone (3:5620).]

[For prepn. of  $\bar{C}$  from chloral (3:5210) (1) (2) (4) or chloral hydrate (3:1270) (3) with diazomethane in ether (yields: 64% (2), 48% (4), 47.5% (3)) see indic. refs.]

$\bar{C}$  does not (2) react with aq. *o*-nitrophenylhydrazine HCl or with aq. semicarbazide.

[ $\bar{C}$  with 5 pts. conc. aq. HCl evolves heat and by opening of epoxy ring yields (2) 1,1,1,3-tetrachloropropanol-2 (3:9030), h.p.  $95-96^\circ$  at 17 mm. (2). —  $\bar{C}$  with  $Ac_2O$  + trace sublimed  $FeCl_3$  gives (2) in analogous fashion 3,3,3-trichloro-1,3-diacetoxypropane, b.p.  $126-128^\circ$  at 16 mm. (2).]

[ $\bar{C}$  with alcohols gives (3) corresp. alkoxymethyl-hemiacetals of chloral.]

[ $\bar{C}$  with  $MeMgI$  in dry ether at  $-15^\circ$  gives (59% yield (4)) 1,1,1-trichloro-3-iodopropanol-2, ndls. from pet. ether, m.p.  $54-55^\circ$  (4). —  $\bar{C}$  with  $MeLi$  in dry ether at  $-75^\circ$  gives (85% yield (4)) 1,1,1-trichlorobutanol-2 (3:5955).]

3:5760 (1) Schlotterbeck, *Ber.* **42**, 2561 (1909). (2) Arndt, Amende, *Ber.* **61**, 1121-1122 (1928). (3) Meerwein, Bersin, Burnelcit, *Ber.* **62**, 1002-1003, 1006-1009 (1929). (4) Gilman, Abbott, *J. Org. Chem.* **8**, 227-228 (1943). (5) von Auwers, *Ber.* **62**, 1319 (1929).

3:5765 METHYL  $\beta$ -CHLOROPROPIONATE  $C_4H_7O_2Cl$  Beil. II - 250  
 $ClCH_2CH_2CO.O.CH_3$   $\Pi_1$ —  
 $\Pi_2$ -(227)

B.P. $148-150^\circ$ at 760 mm. (1)	$D_{44}^{20} = 1.1634$ (7)	$n_D^{20} = 1.4265$ (7)
$148^\circ$ (2)		
$40-42^\circ$ at 10 mm. (3)	$D_{44}^{12} = 1.1874$ (1)	$n_D^{12} = 1.4319$ (1)

[For prepn. of  $\bar{C}$  from  $\beta$ -chloropropionic ac. (3:0470) by esterification with  $MeOH$  +  $HCl$  see (2) (3); from acrylic acid chloride (3:7153) +  $MeOH$  see (2) (4), from methyl



acrylate (1:3025) by addn. of  $\text{HCl}$  see (1), from acrylonitrile +  $\text{HCl}$  to  $\beta$ -chloropropionitrile followed by reactn. with  $\text{MeOH}$  (96% yield (5)) see (5).]

[Note that the b.p. of  $155\text{--}157^\circ$  reported by (4) has been characterized as erroneous (2) (1).]

$\bar{\text{C}}$  on litg. with diethylaniline at abt.  $200^\circ$  gives (1) (78% yield (3)) methyl acrylate (1:3025), b.p.  $80^\circ$  (1).

[For study of acid hydrolysis of  $\bar{\text{C}}$  see (6).]

3:5765 (1) Moureu, Murat, Tampier, *Ann. chim.* (9) 15, 214 (1921). (2) Moureu, *Ann. chim.* (7) 2, 170-171 (1894). (3) Späth, Splitzky, *Ber.* 58, 2276 (1925). (4) Henry, *Compt. rend.* 100, 116 (1885); *J. prakt. Chem.* (2) 31, 127 (1885). (5) British (to I.G.) 352,802, Aug. 6, 1931; *Cent.* 1931, II 2658. (6) Palomaa, *Ber.* 74, 1800-1870 (1941); *C.A.* 36, 5413 (1942). (7) Schlanberg, *Z. physik. Chem. A*-172, 231 (1935).

3:5770 **CYCLOHEXYL CHLOROFORMATE**  $\text{C}_7\text{H}_{11}\text{O}_2\text{Cl}$  Beil. S.N. 199  
(Cyclohexyl chlorocarbonate)  $\text{C}_6\text{H}_{11}\text{O.CO.Cl}$

B.P. abt.  $150^\circ$  dec. (1)

$D_{20}^{20} = 1.1259$  (1)

$87.5^\circ$  at 27 mm. (1)

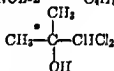
$78\text{--}83^\circ$  at 12 mm. (2)

[For prepn. from cyclohexanol (1:6415) + phosgene (3:5000) see (1); for application in prepn. of textile auxiliaries see (3).]

① Cyclohexyl carbamate: from  $\bar{\text{C}}$  + conc. aq.  $\text{NH}_4\text{OH}$ ; m.p.  $110^\circ$  (2).

3:5770 (1) Kretov, Bakakina, *Zhur. Priklad. Khim.* 2, 809-816 (1929); *C.A.* 24, 1008 (1930); *Cent.* 1930, I 2876. (2) Puyal, Montagne, *Bull. soc. chim.* (4) 27, 802 (1920). (3) French 721,405, Sept. 2, 1932; *Cent.* 1933, I 313.

3:5772 **1,1-DICHLORO-2-METHYLPROPANOL-2**  $\text{C}_4\text{H}_8\text{OCl}_2$  Bell. I - 382  
(*unsym.*-Dichloro-*ter*-butyl alcohol,  
dichloromethyl-dimethyl carbinol)



I—  
I₂—

B.P.

M.P.

$151^\circ$  (1)

$+8^\circ$  (4)

$D_4^{20} = 1.2363$  (4)

$n_D^{20} = 1.4598$  (4)

$150.5^\circ$  at 760 mm. (2)

$143.5^\circ$  (3)

$D_4^{20} = 1.2597$  (4)

$52^\circ$  at 10 mm. (4)

$38^\circ$  at 5 mm. (4)

[See also the isomeric 1,3-dichloro-2-methylpropanol-2 (3:5977).]

### PREPARATION OF $\bar{\text{C}}$

[For prepn. of  $\bar{\text{C}}$  from 1-chloro-2-methylpropene-1 ( $\beta,\beta$ -dimethylvinyl chloride = "isocrotyl chloride") (3:7120) by addn. of  $\text{HOCl}$  with  $\text{Cl}_2$  + aq., aq.  $\text{HOCl}$ , or even alkyl or alkaryl hypochlorites as directed see (2) cf. (5) (3).]

[For prepn. of  $\bar{\text{C}}$  from  $\alpha,\alpha$ -dichloroacetone (3:5430) with  $\text{MeMgBr}$  in ether see (1).]

[For prepn. of  $\bar{\text{C}}$  from ethyl dichloroacetate (3:5850) with  $\text{MeMgBr}$  (74% yield (4)) or  $\text{MeMgI}$  (63% yield (6)) cf. (4) or from methyl dichloroacetate (3:5655) with  $\text{MeMgBr}$  (7) see indic. refs.]

CHEMICAL BEHAVIOR OF  $\bar{C}$ 

With inorganic reagents.  $\bar{C}$  does not (1) react with aq. HCl. —  $\bar{C}$  cannot (4) be hydrolyzed to the corresp. aldehyde, viz.,  $\alpha$ -hydroxyisobutyraldehyde [Beil. I-829, I<sub>2</sub>-(871)], either by aq., aq.  $\text{Na}_2\text{CO}_3$ , aq.  $\text{CaCO}_3$ , or aq.  $\text{PbO}$ .

[ $\bar{C}$  with 5 N ahs. alc.  $\text{NH}_3$  in s.t. nt  $100^\circ$  as directed gives (8) 2,2,5,5-tetramethyldihydropyrazine, m.p.  $83-84^\circ$  (8) (9).]

With organic reactants. [For behavior of  $\bar{C}$  with  $\text{MeNH}_2$  yielding a prod. of compn.  $\text{C}_{16}\text{H}_{32}\text{N}_4$  see (8).]

[ $\bar{C}$  with  $\text{Me}_2\text{NH}$  in  $\text{C}_6\text{H}_6$  in s.t. at  $130^\circ$  not only introduces the dimethylamino group for one chlorine but also ring-closes with loss of HCl giving (52% yield (8)) 1-(dimethylamino)-2-methyl-1,2-epoxypropane ( $\alpha,\alpha$ -dimethyl- $\alpha'$ -(dimethylamino)ethylene oxide), h.p.  $28-30^\circ$  at 13 mm.,  $D_{25}^{25} = 0.8725$ ,  $n_D^{25} = 1.4216$  (8).]

—  $\alpha$ -Hydroxyisobutyraldehyde di- $\beta$ -naphthylacetal [ $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{O.C}_{10}\text{H}_7)_2$ ]: [This cpd. which might be expected from  $\bar{C}$  with sodium  $\beta$ -naphtholate is unreported; note that 1,3-dichloro-2-methylpropanol-2 (3-5977) with sodium  $\beta$ -naphtholate gives the corresp. di- $\beta$ -naphthyl ether, m.p.  $151-152^\circ$ .]

— unsym.-Dichloro-*ter*-butyl acetate: unreported.

— unsym.-Dichloro-*ter*-butyl benzoate: unreported.

— unsym.-Dichloro-*ter*-butyl *p*-nitrobenzoate: unreported.

— unsym.-Dichloro-*ter*-butyl 3,5-dinitrobenzoate: unreported.

— unsym.-Dichloro-*ter*-butyl carbamate: m.p.  $122^\circ$  (7). [Prepd. from unsym.-dichloro-*ter*-butoxy  $\text{MgBr}$  by treatment with phosgene (3:5000) followed by  $\text{NH}_4\text{OH}$  (7).]

(1881). (4) Ayy, *Bull. soc. chim.* (4) 49, 12-18 (1931). (5) Burgin, Hearne, Rust, *Ind. Eng. Chem.* 33, 385-388 (1941). (6) Iositch, *J. Russ. Phys.-Chem. Soc.* 36, 1551 (1906). (7) Yoder, *J. Am. Chem. Soc.* 45, 478-479 (1923). (8) Ayy, *Bull. soc. chim.* (4) 49, 514-522 (1931). (9) Conant, Aston, *J. Am. Chem. Soc.* 50, 2788 (1928).

3:5775 2,2,2-TRICHLOROETHANOL-1  $\text{Cl}_3\text{C.CH}_2\text{OH}$   $\text{C}_2\text{H}_5\text{OCl}_3$  Beil. I - 338  
( $\beta,\beta,\beta$ -Trichloroethyl alcohol) I<sub>1</sub>-(170)  
I<sub>2</sub>-(337)

B.P.		M.P.	
151°	cor. (1)	18° (5)	$D_{23.5}^{23.5} = 1.5500$ (2)
151°	at 737 mm. (2)	17° (6)	
151°	sl. dec. (3)		
149.5-150.5°	at 765 mm. (4)		
149-150°	at 760 mm. (4)		
148-150°	at 720 mm. (5)		
111°	at 170 mm. (6)		
94-97°	at 125 mm. (3)		
67-68°	at 25 mm. (7)		
58-60°	at 16 mm. (8)		
55-56°	at 11 mm. (9)		
52-51°	at 10 mm. (10)		

Colorless when pure, but slightly brown if distilled at ord. press. — Sol. in 12 pts. aq., vol. with steam; miscible with alc. or ether. — Solid is very hygroscopic.

$\bar{C}$  is an important pharmaceutical. — [Although full consideration of its pharmacology is beyond the scope of this text, for studies and reviews of this aspect see (11) (12) (13) (14) (40).] —  $\bar{C}$  in the organism is in part excreted (15) (15) as urochloralic acid [Beil. I-620].

### PREPARATION OF $\bar{C}$

$\bar{C}$  is readily obtd. from trichloroacetaldehyde (chloral) (3:5210) by various types of reducing actions which are able to effect reduction of the aldehyde group without serious interference with the halogen atoms.

By use of various alcoholates. [For prepn. of  $\bar{C}$  from chloral (3:5210) with  $Al(OEt)_3$  in abs. EtOH (yields: 85% (17), 84% (3), 80% (18)) (5) (10) (19) cf. (23) see indic. refs.; with Al isopropylate in isopropyl alc. (20) in pres. of acetaldehyde (yield 72-87% (21)) see indic. refs.; with  $C_2H_5OMgBr$  (9),  $(CH_3)_2CHOMgBr$  (9), or other metallic isopropylates (22) see indic. refs.]

By use of  $RMgX$ . [For formn. of  $\bar{C}$  from chloral (3:5210) during reaction with  $MeMgBr$  (24), with  $EtMgBr$  (25) (4), with iso- $AmMgBr$  (4), with cyclohexyl  $MgBr$  (26), and various other  $RMgBr$  cpds. (7) (25) (yields: 65% (25), 50-60% (4), 42-52% (26)) see indic. refs.]

By use of metal alkyls. [For formn. of  $\bar{C}$  from chloral (3:5210) by use of  $ZnEt_2$  (2) (27) or  $AlEt_3$  cpd. with ether (88.5% yield (8)) see indic. refs.; note, however, that  $SnEt_4$  is not (8) effective.]

By phytochemical agents. [For prepn. of  $\bar{C}$  from chloral (3:5210) by reduction with fermenting yeast see (28) (5).]

By misc. methods. [For formn. of  $\bar{C}$  from urochloralic acid [Beil. I-620] by hydrolysis with dil. mineral acid see (1); for formn. of  $\bar{C}$  in small amts. from EtOH +  $Cl_2$  see (29).]

### CHEMICAL BEHAVIOR OF $\bar{C}$

#### WITH INORGANIC REACTANTS

**Oxidation.**  $\bar{C}$  reduces Fehling's soln. on warming (2). —  $\bar{C}$  with fuming  $HNO_3$  is oxidized to trichloroacetic acid (1) (2).

**Behavior with alkalis.** [ $\bar{C}$  in conc. aq. NaOH first dissolves then gives a white ppt. of Na deriv. (33). —  $\bar{C}$  with aq. KOH dissolves and soon afterward reacts vigorously yielding (2) various prods. including chloroacetic acid (3:1370),  $\beta,\beta,\beta$ -trichloroethoxyacetic acid [Beil. III-233], m.p. 69.5° (2), and formic acid (1:1005).]

**Behavior with inorganic acid chlorides.** [ $\bar{C}$  with  $PCl_3$  evolves HCl and yields (27) *tris*-( $\beta,\beta,\beta$ -trichloroethyl) phosphite, b.p. 263°, no formation of 1,1,1,2-tetrachloroethane (3:5555) being evident. —  $\bar{C}$  with  $PCl_5$  at 140° evolves HCl yielding (27) *tris*-( $\beta,\beta,\beta$ -trichloroethyl) phosphate, m.p. 73-74° (sublimes without decn.) accompanied by a trace of 1,1,1,2-tetrachloroethane (3:5555).]

[ $\bar{C}$  with  $SOCl_2$  gives (30) *bis*-( $\beta,\beta,\beta$ -trichloroethyl) sulfite, b.p. 139.5-140° at 5 mm., m.p. 6-7°. —  $\bar{C}$  with  $SO_2Cl_2$  in pyridine at 100° gives (30) *bis*-( $\beta,\beta,\beta$ -trichloroethyl) sulfate, m.p. 118.5-119.5° cor., also obtd. (30) by oxidn. of the preceding sulfite with acid  $KMnO_4$  in acetone.]

**Behavior with  $AlBr_3$ .** [ $\bar{C}$  with  $AlBr_3$  in  $CS_2$  (31) (32) undergoes replacement of chlorine by bromine yielding acc. to conditions  $\beta$ -bromo- $\beta,\beta$ -dichloroethanol, m.p. 17.5 (32), m.p. 17.5° (32), or  $\beta,\beta$ -dibromo- $\beta$ -chloroethanol, m.p. 50°, b.p. 80° at 8 mm. (32).]

## WITH ORGANIC REACTANTS

(See also below under derivatives.) — [ $\bar{C}$  with diazomethane in heptane (33), *n*-BuOH (34), or acetone (33) (but not in ether (33)), yields  $\beta,\beta,\beta$ -trichloroethyl methyl ether, b.p. 35–36° at 16 mm. (33).]

[ $\bar{C}$  with 2,3-dichlorodioxane-1,4 (3:9105) gives (50% yield (18)) 2-chloro-3-( $\beta,\beta,\beta$ -trichloroethoxy)dioxane-1,4, m.p. 77–78°.]

[ $\bar{C}$  with  $BEt_3$  at 150° evolves  $C_2H_6$  and gives (44% yield (8))  $\beta,\beta,\beta$ -trichloroethyl diethylborate,  $CCl_3CH_2OB(C_2H_5)_2$ , b.p. 78–79° at 12 mm. (8).]

—  $\beta,\beta,\beta$ -Trichloroethyl acetate: oil, b.p. 167° sl. dec. at 736 mm. (2), 71° at 18.3 mm. (2), 88–91° (35),  $D_4^{25} = 1.4239$  (35),  $n_D^{25} = 1.4691$  (35). [From  $\bar{C}$  with  $AcCl$  in *s.t.* at 130° for several hrs. (2).]

—  $\beta,\beta,\beta$ -Trichloroethyl benzoate: oil (29). [Note, however, that no constants are reported in the literature.]

①  $\beta,\beta,\beta$ -Trichloroethyl *m*-nitrobenzoate: m.p. 75° (29) (26). [From  $\bar{C}$  + *m*-nitrobenzoyl chloride + aq. alk. (29).]

②  $\beta,\beta,\beta$ -Trichloroethyl *p*-nitrobenzoate: m.p. 71° (28) (25). [From  $\bar{C}$  + *p*-nitrobenzoyl chloride + aq. alk. (28).]

③  $\beta,\beta,\beta$ -Trichloroethyl 3,5-dinitrobenzoate: m.p. 142–143° (25).

④  $\beta,\beta,\beta$ -Trichloroethyl carbamate: m.p. 64–65° (28) (36) (37) (38), 64° (39). [From  $\bar{C}$  (1 mole) with carbamyl chloride (1 mole) in dry ether (28) (note that  $\bar{C}$  with excess of carbamyl chloride gives (28)  $\beta,\beta,\beta$ -trichloroethyl allophanate, m.p. 182–183°), or from  $\bar{C}$  by treatment with phosgene (3:5000) followed by  $NH_3$  (37). — Note that this prod. comprises the hypnotic pharmaceutical known as "Voluntal." It also forms molecular cpds. with various other pharmaceuticals; e.g., "Voluntal," m.p. 64–65° + pyrazolone (2,3-dimethyl-4-dimethylamino-1-phenyl-pyrazolone-5) [Beil. XXV-452, XXV<sub>1</sub>-(672)], m.p. 108°, give a 1:1 mol. cpd., m.p. 75–76°, known as "Compral"; for f.p./compn. data and diagrams see this (and similar systems) see (39).]

—  $\beta,\beta,\beta$ -Trichloroethyl *N*-phenylcarbamate: m.p. 87° (39). [For f.p./compn. data and diagrams of this prod. (also known as *N*-phenylvoluntal) with atipyrine, etc., see (39).]

⑤  $\beta,\beta,\beta$ -Trichloroethyl *N*-( $\alpha$ -naphthyl)carbamate: m.p. 120° (7), 119° (26). [From  $\bar{C}$  +  $\alpha$ -naphthyl isocyanate at 120–135° for 2 hrs. (7).]

3:5775 (1) von Mering, *Z. physiol. Chem.* 6, 487 (1882). (2) Carzarolli-Thurnlackh, *Ann.* 210, 64–68 (1881). (3) Chalmers, *Org. Syntheses*, Coll. Vol. 2 (1st ed.), 598–601 (1943); 15, 80–84 (1935). (4) Jotsitch, *J. Russ. Phys.-Chem. Soc.* 36, 443–446 (1904), *Bull. soc. chim.* (3) 34, 329–330 (1905). (5) Lintner, *Löers, Z. physiol. Chem.* 88, 122–123 (1913). (6) Callen (to Winthrop Chem. Co.), U.S. 1,725,054, Aug. 20, 1929; (*Cent.* 1930, 1 434), *C.A.* 23, 4709 (1929); *Cer.* 437,160, Nov. 18, 1926; *Cent.* 1927, 1 802; not in *C.A.*: *Brit.* 286,797, April 5, 1928; *Cent.* 1929, 1 2750, *C.A.* 23, 395 (1929). (7) Dean, Wolf, *J. Am. Chem. Soc.* 58, 332–333 (1936). (8) Meerwein, Hinz, Majert, Sönke, *J. prakt. Chem.* (2) 147, 236, 243 (1936). (9) Callen (to I.G.), *Cer.* 565,157, Nov. 26, 1932; *Cent.* 1933, 1 1514; *C.A.* 27, 992 (1933); *Brit.* 384,156, Dec. 22, 1932; *Cent.* 1933, 1 1351; [*C.A.* 27, 4240 (1933)]. (10) Nakai, *Biochem. Z.* 152, 272 (1924); *Cent.* 1925, 1 637, [*C.A.* 19, 2807 (1925)].

1097]; *C.A.* 20, 917 (1926). {20} Callsen (to I.G.), *Ger.* 489,281, Jan. 15, 1930; *Cent.* 1930, I 1929, I 1741; *C.A.* 23, 852 (1929). in *C.A.* {22} I.G., *Brit.* 370,490, {23} Dworzak, *Monatsh.* 47, 12-tem. *Soc.* 63, 2306-2307 (1941). Floutz, *J. Am. Chem. Soc.* 65, 2255 (1943). {27} Delacre, *Bull. soc. chim* (2) 48, 784-788 (1887). {28} Willstätter, *Duisberg, Ber.* 56, 2284-2285 (1923). {29} Altschul, Meyer, *Ber.* 26, 2758 (1893). {30} Sporzynski, *Arch. Chem. Farm.* 2, 243-247 (1935); *Cent.* 1935, II 2941; *C.A.* 30, 5938 (1936). {31} Muller (to Winthrop Chem. Co.), U.S. 2,057,964, Oct. 20, 1936; *C.A.* 31, 112 (1937); not in *Cent.*: *Brit.* 366,581, March 3, 1932; *Cent.* 1932, II 770; [*C.A.* 27, 1893 (1933)]. {32} Schranz, Göth, Kühn, Kayser, *Ger.* 600,769, July 31, 1934; *Cent.* 1934, II 2285; [*C.A.* 28, 7429 (1934)]. {33} Meerwein, Bersin, Burneleit, *Ber.* 62, 1006-1007 (1929). {34} Meerwein, Hinz, *Ann.* 484, 23 (1930). {35} Baum, Vogt, Hennion, *J. Am. Chem. Soc.* 61, 1458 (1939). {36} Willstätter, Straub, Hauptmann, *Munch. med. Wochschr.* 69, 1651-1654 (1922); *Cent.* 1923, I 1196; not in *C.A.* {37} F. Bayer & Co., *Ger.* 358,125, Sept. 4, 1922; *Cent.* 1922, IV 888; *C.A.* 17, 2172 (1923). {38} Mentzel, *Pharm. Zentralhalle* 63, 579-580 (1922); 64, 10-11 (1923); *Cent.* 1923, II 549. {39} Pfeiffer, Seydel, *Z. physiol. Chem.* 178, 81-96 (1928). {40} Burtner, Lehmann, *J. Pharmacol.* 63, 183-192 (1938); *C.A.* 32, 6741 (1938).

3:5780  $\beta$ -CHLOROETHYL CHLOROFORMATE  $C_2H_5O_2Cl_2$  Beil. III - 11  
( $\beta$ -Chloroethyl chlorocarbonate)  $ClCH_2CH_2O.CO.Cl$  III—  
III-(10)

B.P. 152.5° at 752 mm. (1)  $D_4^{20} = 1.3825$  (1)  $n_D^{20} = 1.4465$  (1)

Colorless lachrymatory liq. which fumes in air. — Insol. nq., eas. sol. alc., ether.

[For prepn. from  $\beta$ -chloroethanol (ethylene chlorohydrin) (3:5552) + phosgene (3:5000) see (1).]

$\bar{C}$  on slight warming with quinoline dec. at 41-42° into ethylene dichloride (3:5130) +  $CO_2$  (2).

$\bar{C}$  is readily hydrolyzed by warm aq. or dil. alk. to  $\beta$ -chloroethanol (3:5552) +  $CO_2$  + HCl (1).

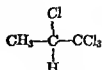
①  $\beta$ -Chloroethyl carhamate: from  $\bar{C}$  + 2 moles conc. aq.  $NH_4OH$ ; m.p. 76° (3) (4) (5). [The value of 115° given in Beil. III-11 is wrong (5).]

②  $\beta$ -Chloroethyl *N*-phenylcarhamate: from  $\bar{C}$  in  $C_6H_6$  added to  $C_6H_6$  soln. of aniline (2 moles); after filtering off the pptd. aniline hydrochloride, the  $C_6H_6$  is evapd. (6); white ndls., m.p. 51° (3). [This deriv. on short boilg. with dil. aq. or alc. alk. loses HCl and by ring closure yields 3-phenyloxazolidone-2 [Beil. XXVII-136], lfts. from alc., m.p. 124° (3), 122° (7).]

③  $\beta$ -Chloroethyl *N*-*p*-tolylcarhamate: white ndls. from  $C_6H_6$ , m.p. 45° (6). [On treatment with alk. this gives 3-(*p*-tolyl)oxazolidone-2, white ndls. from alc., m.p. 91° (6).]

④  $\beta$ -Chloroethyl phenylcarbazate: from  $\bar{C}$  on treatment with 1 mole phenylhydrazine in aq. pyridine; the red oil initially formed soon solidifies and is recrystd. from  $C_6H_6$ ; white ndls., m.p. 89° (8).

3:5780 (1) Nekrassow, Komissarow, *J. prakt. Chem.* (2) 123, 163 (1929). (2) Garré, *Bull. soc. chim.* (5) 3, 1069 (1936). (3) Nemirowsky, *J. prakt. Chem.* (2) 31, 174-175 (1885). (4) *Ger.* 387,963, Jan. 1, 1924; *Cent.* 1924, II 403. (5) Kuroda, *Cent.* 1927, II 243. (6) Adams, Segur, *J. Am. Chem. Soc.* 45, 787-789 (1923). (7) Otto, *J. prakt. Chem.* (2) 44, 17 (1891). (8) Dox, *J. Am. Chem. Soc.* 48, 1952 (1926).

**3:5785 1,1,1,2-TETRACHLOROPROPANE**  
 ( $\beta, \beta, \beta$ -Trichloroisopropyl chloride)
 $\text{C}_3\text{H}_4\text{Cl}_4$  Beil. I - 107
 $\text{I}_1 -$   
 $\text{I}_2 -$ 

B.P.	F.P.		
152-153° cor. at 760 mm. (1)	-65° (1)	$D_{15}^{22} = 1.4695$ (6)	$n_D^{20} = 1.4855$ (6)
150-151° at 751 mm. (6)	-64° (6)	$D_{20}^{20} = 1.473$ (1)	$n_D^{20} = 1.4867$ (1)
87-88° nt 104 mm. (6)			

Colorless liq. insol. nq. [For use as dry-cleaning solvent see (2).]

 [For prepn. of  $\bar{C}$  from 1,1,1-trichloropropanol-2 (3:0846) via reactn. with  $\text{PCl}_3$  and action of  $\text{Cl}_2$  on this product see (1), for prepn. of  $\bar{C}$  with 1,1-dichloropropene-1 (3:5120) +  $\text{Cl}_2$  + cat at 0-30° in absense of light see (3) (4); from 3,3,3-trichloropropene-1 (3:5345) by addn. of  $\text{HCl}$  in pres. of 3%  $\text{FeCl}_3$  in s.t. at 50° for 50-100 hrs. see (6).]

 $\bar{C}$  with aq. or nlc.  $\text{NaOH}$  or  $\text{KOH}$  for 3 hrs. at 95° gives (93% yield (5)) 1,1,2-trichloropropene-1 (3:5395), b p. 118° (5).

 3:5785 (1) Henry, *Rec. trav. chim.* 24, 333-334 (1905). (2) Schmitt, *Ber.* 38, 2010-2020 (1905). (3) Cass (to du Pont Co.), *Cent.* 1935, 11 3859, C.A. 29, 6410 (1935). (4) du Pont Co. & (5) du Pont Co. & (6) Kharasch, *Res.* 2359-2560 (1941).

**3:5800 METHYL TRICHLOROACETATE**
 $\text{C}_2\text{H}_3\text{O}_2\text{Cl}_3$ 

Beil. II - 208


 $\text{II}_1 -$   
 $\text{II}_2 - (100)$ 

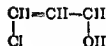
B.P.	F.P.		
153.8° at 760 mm. (1)	-17.5° (1)	$D_4^{20} = 1.4874$ (8)	$n_D^{20} = 1.4572$ (8)
153° (2)		1.4864 (7)	1.45717 (7)
152.3-152.5° at 765.3 mm. (3)			
150.0-150.5° at 679 mm. (4)			
52-54° at 12 mm. (5)			
41.5-41.6° at 12 mm. (6)			
46.5-47.0° at 11 mm. (7)			

 [For prepn. of  $\bar{C}$  from trichloroacetic acid (3:1150) with  $\text{MeOH}$  nt 60° (50-66% yield (2)), with  $\text{MeOH} + \text{HCl}$  at 50° (74.6% yield (2)), with  $\text{MeOH} + \text{H}_2\text{SO}_4$  (9), with  $\text{MeOH} + \text{BF}_3 \cdot \text{Et}_2\text{O}$  at 61° (73% yield (2)), or with  $\text{Me}_2\text{SO}_4$  in s.t. at 200° (10) see indic. refs.; from trichloroacetamide +  $\text{MeOH} + \text{BF}_3$  (53% yield) see (2); from "tetrachloroethylidene trichlorolactate" [Beil. XIX-105] with  $\text{MeOH}$  see (5).]

 [For studies on hydrolysis of  $\bar{C}$  under various circumstances see (11) (6) (7) (12)]

[For speed of reactn. with pyridine nt 18-20° see (13).]

 3:5800 (1) Henry, *Rec. trav. chim.* 24, 333-334 (1905). (2) Schmitt, *Ber.* 38, 2010-2020 (1905). (3) Trole, Sowa, *J. Am. Chem. Soc.* 57, 1111-1112 (1935). (4) Sudborough, Karve, (5) Aneshkin, Haxham, (6) Salomon, Salmi, Korte, (7) Dumas, *Ber.* 72, 790-797 (1939). (8) Schjaneberg, *Z. physik. Chem.* A-172, 229 (1935). (9) Dumas, *Ann.* 32, 111 (1839). (10) Simon, *Compt. rend.* 176, 5-3 (1923). (11) Olivier, Berger, *Rec. trav. chim.* 41, 612 (1921); 44, 643, 647-648 (1925). (12) Salmi, *Suomen. Ber.* 73, 1126-1131 (1940). (13) Tronov, Akisik, Orlova, *J. Russ. Phys.-Chem. Soc.* 61, 345-353 (1929); *Cent.* 1929, 11 2550; C.A. 24, 590 (1930).

**3:5820 3-CHLOROPROPEN-2-OL-1**  
 ( $\gamma$ -Chloroallyl alcohol)


Bell. I - 139

I<sub>1</sub>—I<sub>2</sub>—

High-boiling stereoisomer B.P. 153.0° at 756 mm. (1)

$D_{15}^{25} = 1.1582 \text{ (1)} \quad n_D^{25} = 1.4600 \text{ (1)}$

$D_{15}^{25} = 1.1681 \text{ (1)} \quad n_D^{25} = 1.4611 \text{ (1)}$

$D_{15}^{20} = 1.1720 \text{ (1)} \quad n_D^{20} = 1.4601 \text{ (1)}$

Low-boiling stereoisomer B.P. 146.3° at 746 mm. (1)

$D_{15}^{25} = 1.1623 \text{ (1)} \quad n_D^{25} = 1.4573 \text{ (1)}$

$D_{15}^{25} = 1.1720 \text{ (1)} \quad n_D^{25} = 1.4617 \text{ (1)}$

$D_{15}^{20} = 1.1760 \text{ (1)} \quad n_D^{20} = 1.4638 \text{ (1)}$

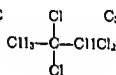
Colorless liquids; both stereoisomers possess a delayed vesicant notn., and care should be taken in handling them.

[For prepn. of  $\bar{O}$  from 1,3-dichloropropene-1 ( $\gamma$ -chloroallyl chloride) (3:5256) by hydrolysis for 2 hrs. under reflux with aq. 10%  $\text{Na}_2\text{CO}_3$  (10% excess over 1 equiv.) see (1); note that the high-boiling stereoisomer of  $\gamma$ -chloroallyl chloride gives (76% yield) of the high-boiling  $\bar{O}$ , and that the lower-boiling stereoisomer of  $\gamma$ -chloroallyl chloride gives (81% yield) the lower-boiling stereoisomer of  $\bar{O}$  (1).—Note that from  $\gamma$ -chloroallyl acetate (which was presumably a mixture of the acetates of both stereoisomers of  $\bar{O}$ ) by hydrolysis with cold aq.  $\text{NaOH}$   $\bar{O}$  (presumably a mixt. of stereoisomers) has been reported (2).]

The two stereoisomers of  $\bar{O}$  behave differently with hot aq.  $\text{NaOH}$  (1): the higher-boiling stereoisomer fails to give any propargyl alcohol but some acetylene and sodium formate are formed; the lower-boiling stereoisomer on refluxing with aq. 12.5%  $\text{NaOH}$  (10% excess) for 3 hrs. gives (by dehydrochlorination) 69% yield of propargyl alcohol (propyne-1-ol-3) [Bell. I-151], b.p. 114–115° (for study of influence of  $\text{NaOH}$  concn. and time see (1)).

①  $\gamma$ -Chloroallyl *N*-phenylcarbamate: ndls. from pet. ether, m.p. 75° (2). [From  $\bar{O}$  + phenyl isocyanate (note, however, that the  $\bar{O}$  employed very probably was a mixt. of the two stereoisomers (2)).]

3:5820 (1) Hatch, Moore, *J. Am. Chem. Soc.* 60, 285–287 (1938). (2) Kirmann, Prenud, Dosque, *Bull. soc. chim.* (3) 1, 863 (1931).

**3:5825 1,1,2,2-TETRACHLOROPROPANE**


Bell. I - 107

I<sub>1</sub>—I<sub>2</sub>—
 B.P. 153–154° (1)  
 153° (3)

$D_{15}^{25} = 1.47 \text{ (1)}$

Liquid; misc. with alc. or ether; insol. aq.

[For prepn. of  $\bar{O}$  from  $\alpha,\alpha$ -dichloroacetone (3:5136) +  $\text{PCl}_5$  see (3); from 1,2-dichloropropene-1 (3:5150) by addn. of  $\text{Cl}_2$  see (1); for forma. of  $\bar{O}$  in small amt. as by-product of octa. of  $\text{Cl}_2$  on propylene see (2).]

$\bar{O}$  with warm alc.  $\text{KOH}$ , or with alc.  $\text{NH}_3$  at 140° splits off  $\text{HCl}$  yielding (3) (1) 1,1,2(?)-trichloropropene-1, (3:5395), b.p. 115° (3), 116–117° (1).

3:5825 (1) Szencle, Taggesell, *Ber.* 28, 2067–2068 (1895). (2) Goudet, Schenker, *Helv. Chim. Acta* 10, 136 (1927). (3) Barache, *Fittig. Ann.* 133, 111–117 (1865).

3:5835	1,4-DICHLOROBUTANE (Tetramethylene (di)chloride)	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ $\begin{array}{c}   \\ \text{Cl} \end{array} \quad \begin{array}{c}   \\ \text{Cl} \end{array}$	$\text{C}_4\text{H}_8\text{Cl}_2$	Beil. I - 119 I <sub>1</sub> -( 38) I <sub>2</sub> -( 81)
B.P.		M.P.		
155°	at 760 mm. (1) (6)	-38.7° (4)	$D_4^{20} = 1.1598$ (2)	$n_D^{20} = 1.4566$ (2)
74.7°	at 50 mm. (2)			
53-58°	at 12 mm. (3)			

The b.p. of 163° (3) is erroneous (1).

[For prepn. from *N*-benzoylpyrrolidine [Beil. XX-5] +  $\text{PCl}_5$  see (3); from *N,N'*-dibenzoyltetramethylenediamine +  $\text{PCl}_5$  see (5); from butanediol-1,4 (tetramethylene glycol) (1:6516) +  $\text{SOCl}_2$  see (10); from 1-chlorobutane by chlorination in light (together with other products) see (2) (7) (8) (9); from tetrahydrofuran [Beil. XVII-10, XVII-(5)] with  $\text{HCl}$  gas in pres. of 50%  $\text{ZnCl}_2$  (59% yield) see (15) [note that in absence of  $\text{ZnCl}_2$  only 4-chlorobutanol-1 (3:9170) is formed (15) (16).]

[ $\text{C}$  on passing over alkali ( $\text{NaOH}$ ,  $\text{K}_2\text{CO}_3$ , soda-lime, etc.) at elevated temperatures (e.g., 700-750°) yields butadiene-1,3.] [For studies of this reaction see (7) (8) (9).]

$\text{C}$  can be hydrolyzed to tetramethylene glycol (1:6516) only very slowly (6).

$\text{C}$  ltd. with *p*-toluidine (3 moles) at 100° for 10 hrs. gives (70% yield (11)) *N-p*-tolylpyrrolidine, b.p. 120° at 8 mm., cryst. from dil. alc., m.p. 42° (11). [For corresp. behavior with aniline yielding *N*-phenylpyrrolidine see (12).]

— 1,4-Diphthalimidobutane: obtd. indirectly (13) and as by-product (14) of prepn. of *N*-(3-chloro-*n*-butyl)phthalimide; pr. from  $\text{AcOH}$ , m.p. 219° (13).

3:5835 (1) Hlasek, *J. Chem. Education* 13, 493 (1936). (2) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 7, 893-890 (1937); *C.A.* 31, 5755 (1937); *Cent.* 1938, 11 2575. (3) von Braun, Beschke, *Ber.* 39, 4361 (1906). (4) Timmermans, *Bull. soc. chim. Belg* 31, 390 (1922). (5) von Braun, Lemke, *Ber.* 55, 3530 (1922). (6) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 9, 1380-1388 (1939), *C.A.* 34, 1611 (1940). (7) Muskat, Northrup, *J. Am. Chem. Soc.* 52, 4050-4052 (1930). (8) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 7, 893-890 (1937). (9) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 9, 1380-1388 (1939). (10) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 9, 1380-1388 (1939). (11) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 9, 1380-1388 (1939). (12) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 9, 1380-1388 (1939). (13) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 9, 1380-1388 (1939). (14) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 9, 1380-1388 (1939). (15) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 9, 1380-1388 (1939). (16) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 9, 1380-1388 (1939).

*m. Chem. Soc.*  
(1939). (14)  
(1941). (16)

3:5840	1,2,3-TRICHLOROPROPANE (Glycerol trichlorohydrin; "trichlorohydrin")	$\text{CH}_2\text{—CH—CH}_2$ $\begin{array}{c}   \\ \text{Cl} \end{array} \quad \begin{array}{c}   \\ \text{Cl} \end{array} \quad \begin{array}{c}   \\ \text{Cl} \end{array}$	$\text{C}_3\text{H}_5\text{Cl}_3$	Beil. I - 106 I <sub>1</sub> -( 31) I <sub>2</sub> -( 73)
B.P.		F.P.		
[158°	(1)]	-1.17° (2)	$D_4^{20} = 1.394$ (7)	$n_D^{20} = 1.4858$ (5)
157°	(6)			
156.85°	(2)		$D_4^{15} = 1.417$ (8)	
156.0°	at 760 mm. (3)			
154-156°	(4)			
154.6-155.6°	at 738 mm. (5)			

[For prepn. of  $\text{C}$  from glycerol (1:6540) with 3 moles  $\text{SOCl}_2$  + 3 moles pyridine at 110-120° (78% yield) see (9); from either 1,3-dichloropropanol-2 (glycerol  $\alpha$ -dichlorohydrin) (3:5955) or 2,3-dichloropropanol-1 (glycerol  $\beta$ -dichlorohydrin) (3:6060) with  $\text{PCl}_5$  see



{10} {11}; from 1,3-dichloropropanol-2 (see above) with  $\text{POCl}_3$  at  $180^\circ$  (but only as byprod.) see {12}, or with  $\text{SOCl}_2$  + diethylaniline see {13}; from allyl chloride (3:7035) with  $\text{Cl}_2$  {6} or with  $\text{SO}_2\text{Cl}_2$  (80-90% yield {14}) see indic. refs.; from allyl iodide {15} or isopropyl iodide {8} {16} with  $\text{Cl}_2$  see indic. refs.; from propane +  $\text{Cl}_2$  see {17} {16}; from 1,2-dichloropropane (propylene dichloride) (3:5200) with  $\text{Cl}_2$  + Fe in ultra-violet light at  $-18^\circ$  {18} {19} or with  $\text{SO}_2\text{Cl}_2$  in pres. of org. peroxides {26} cf. {27} see indic. refs.; from propylene with  $\text{Cl}_2$  in gas phase in dark in absence of Fe see {20}.

$\bar{\text{C}}$  on htg. with 20 pts. aq. in s.t. at  $160^\circ$  {11} or with aq.  $\text{NaHCO}_3$  + Cu under press. at  $130^\circ$  for 5-6 hrs. {21} or with steam over cat. at  $550$ - $850^\circ$  {25} yields glycerol (1:6540).

$\bar{\text{C}}$  on warming with solid KOH loses HCl yielding {22} mainly 2,3-dichloropropene-1 (3:5190) together with some 1,3-dichloropropene-1 (3:5280).

[ $\bar{\text{C}}$  with alc. KSH yields {23} trithioglycerol [Beil. I-519] cf. {24}.]

[ $\bar{\text{C}}$  with  $\text{ShCl}_3$  at  $190^\circ$  yields {6} 1,1,2,3-tetrachloropropane (3:6035).]

3:5840 {1} Carius, *Ann.* 124, 223 (1862). {2} Timmermans, *Bull. soc. chim. Belg.* 30, 67 (1921).

{3} Gibson, *J. Soc. Chem. Ind.* 50, 950 (1931). {4} Herzfelder, *Ber.* 26, 1259 (1893). {5} Kohl-

rausch, Ypsilanti, *Z. physik. Chem.* B-32, 416 (1936). {6} Herzfelder, *Ber.* 26, 2435 (1893).

{7} Blanchard, *Bull. soc. chim.* (4) 43, 1198 (1928). {8} Linneman, *Ann.* 136, 48 (1865). {9}

Carré, Maclere, *Bull. soc. chim.* (4) 49, 1152 (1931). {10} Fittig, *Pfeffer, Ann.* 135, 359 (1865).

{11} Berthelot, *Luca, Jahresber.* 1857, 477. {12} Hill, Fischer, *J. Am. Chem. Soc.* 44, 2588

(1922). {13} Darzens, *Compt. rend.* 152, 1314 (1911). {14} Kharasch, Brown, *J. Am. Chem.*

*Soc.* 61, 3432-3434 (1939). {15} Oppenheim, *Ann.* 133, 383-384 (1865). {16} Berthelot, *Ann.*

155, 103 (1870). {17} Schorlemmer, *Ann.* 152, 159-163 (1869). {18} Cass, Levine (to du Pont

Co.) *Brit.* 471,188, Sept. 30, 1937; *Cent.* 1938, I 1218; *C.A.* 32, 957 (1938). {19} Friedel, *Silva,*

*Zeit. für. Chemie* 1871, 683. {20} Laughlin, Brown (to Standard Oil Development Co.), U.S.

2,300,159, Oct. 27, 1942; *C.A.* 37, 1725 (1943).

{21} Matter, *Ger.* 369,502, Feb. 20, 1923; *Cent.* 1923, II 742. {22} Reboul, *Ann. chim.* (3)

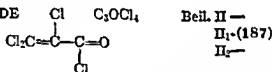
60, 38-40 (1860). {23} Ref. 1, pp. 236-240. {25} Lillienfeld, *Brit.* 385,980, Feb. 2, 1933; *Cent.*

1933, 1928. {26} Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; *Cent.* 1932, I 2994. {26}

Kharasch, Brown, *J. Am. Chem. Soc.* 61, 2145 (1939). {27} Zellner (to Tido Water Associated

Oil Co.) U.S. 2,370,342, Feb. 27, 1945; *C.A.* 39, 3535 (1945).

### 3:5845 TRICHLOROACRYLOYL CHLORIDE



B.P.  $158^\circ$  at 760 mm. {1} {2}

$n_D^{25} = 1.52709$  {2}

[For prepn. of  $\bar{\text{C}}$  from trichloroacrylic acid (3:1840) with  $\text{SOCl}_2$  ( $2\frac{1}{2}$  moles) refluxed for 12 hrs. (80-90% yield) see {2} cf. {6}.]

$\bar{\text{C}}$  with  $\text{AlCl}_3$  in  $\text{CS}_2$  gives {1} n very stable 1:1 addn. prod.; on htg. it does not lose CO but ultimately decomposes giving {1} trichloroacetic acid (3:1150).

$\bar{\text{C}}$  with  $\text{C}_6\text{H}_6$  +  $\text{AlCl}_3$  gives (100% yield {1}) {3} phenyl  $\alpha,\beta,\beta$ -trichlorovinyl ketone [Beil. VII-1(190)], oil, b.p.  $138^\circ$  at 2 mm. {2},  $D_4^{25} = 1.3902$  {2};  $n_D^{25} = 1.5798$  {2}; for analogous behavior of  $\bar{\text{C}}$  with toluene + many other arom. hydrocarbons +  $\text{AlCl}_3$  see {2}.

[ $\bar{\text{C}}$  with 3%  $\text{H}_2\text{O}_2$  + 25% aq.  $\text{NaOH}$  at  $-3^\circ$  to  $0^\circ$  gives (69% yield {3}) *cis*-(trichloroacryloyl) peroxide, cryst. from alc., m.p.  $49^\circ$ .]

① Trichloroacrylic acid amide: m.p.  $97^\circ$  {4},  $96$ - $97^\circ$  {5} aq.  $\text{NH}_4\text{OH}$  {5} or from ethyl trichloroacrylate graphic study see {4}.]

[From  $\bar{\text{C}}$  with  
" - [For ...]

— Trichloroacrylic anilide: ndls. from ppt with aniline (2 moles) in  $\text{CHCl}_3$  at  $0^\circ$  {7}.

from  $\bar{\text{C}}$  {1}

— Trichloroacrylic *p*-toluidide: .

3:5845 (1) Böeseken, Hasselbach, *Rec. trav. chim.* **32**, 10-11 (1913). (2) Böeseken, Dujardin, *Rec. trav. chim.* **32**, 101-111 (1913). (3) Böeseken, Gelissen, *Rec. trav. chim.* **43**, 266-268 (1924). (4) Gilta, *Bull. soc. chim. Belg.* **39**, 587-588 (1930). (5) Fritsch, *Ann.* **297**, 317-318 (1897). (6) Bergmann, Haskelberg, *J. Am. Chem. Soc.* **63**, 1438 (1941).

## 3:5850 ETHYL DICHLOROACETATE



Beil. II - 203



II-(91)

II-(196)

B.P. 158.3-158.7° (1)

158-158.2° cor. (2)

157.7° at 754.6 mm. (3)

157° (4)

156° at 738.2 mm. (5)

154-155° at 749.5 mm. (6)

[For prepn. of  $\bar{C}$  from dichloroacetic acid (3:6208) with EtOH + HCl see (7) (8); from chloral (3:5210) or chloral hydrate diacetate with EtOH/KCN (88% and 80% yield, respectively) see (4); from chloral cyanohydrin with abs. EtOH + conc. KOH (8) or abs. EtOH + anhyd. NaOAc (9) see indic. refs.; from tetrachloroethylene (3:5460) with NaOEt in s.t. at 100-120° see (10); from  $\alpha,\beta$ -dichlorovinyl ethyl ether (3:5540) with  $Cl_2$  followed by aq. see (11); from  $\beta,\beta$ -dichloro- $\alpha$ -acetoxyacrylonitrile with EtOH in s.t. at 150° see (12); for formn. of  $\bar{C}$  in reactn. of EtOH with  $Cl_2$  see (13).]

$\bar{C}$  on boilg. with alc. KOH yields (14) glycolic acid (1:0430) and oxalic acid (1:0445);  $\bar{C}$  on htg. with NaOEt in abs. alc. yields (15) a small amt. ethyl diethoxyacetate together with larger amts. of diethyl oxalo-chloroacetate diethylacetal on its decn. products.

$\bar{C}$  on boilg. with EtOH + KCN yields (16) K dichloroacetate, AcOH, and oxalic acid;  $\bar{C}$  on boilg. with EtOH + KF yields (17) KCl,  $SiF_4$  + ethyl glyoxylate.]

$\bar{C}$  in ether treated with Na or htd. with Ag yields (18) diethyl maleate (1:3791).]

$\bar{C}$  on shaking with aq. + benzylamine yields (19) *N*-benzyl-dichloroacetamide, m.p. 94.8-95.6° cor. (19), 95-96° (20).

$\bar{C}$  on hydrolysis with acid yields EtOH (1:6130) + dichloroacetic acid (3:6208). [For study of kinetics of this hydrolysis see (21) (22) (23).]

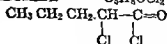
(10) Fischer, Geuther, *Jahresber.* **1864**, 316.

(11) Crompton, Triffitt, *J. Chem. Soc.* **113**, 1874-1875 (1921). (12) Kotz, *J. prakt. Chem.* **103**, 232 (1921/22). (13) Altschul, Meyer, *Ber.* **26**, 2757 (1893). (14) Claus, *Ber.* **14**, 1066 (1881). (15) Cope, *J. Am. Chem. Soc.* **58**, 570-572 (1936). (16) Claus, *Ber.* **11**, 496-498; 1043-1044 (1878). (17) Swarts, *Cent.* **1903**, I 14. (18) Tanatar, *Ber.* **12**, 1564 (1879). (19) Buehler, Mackenzie, *J. Am. Chem. Soc.* **59**, 421-422 (1937). (20) Mannich, Kuphal, *Arch. Pharm.* **250**, 544 (1912).

(21) Newling, Hinshelwood, *J. Chem. Soc.* **1936**, 1357-1361. (22) Timm, Hinshelwood, *J. Chem. Soc.* **1938**, 862-869. (23) Salmi, Suonpaa, *Ber.* **73**, 1126-1131 (1940).

3:5860 *d,l*- $\alpha$ -CHLORO-*n*-VALERYL CHLORIDE

Beil. II - 302



II-

II-

B.P. 155-157° at 763 mm. (1)

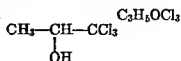
 $D_4^{20} = 1.246$  (1)

[For prepn. of  $\bar{C}$  from  $\alpha$ -chloro-*n*-valeric acid (3:8783) with  $PCl_3$  at 70-80° see (1).]

$\bar{C}$  on hydrolysis with aq. yields (1)  $\alpha$ -chloro-*n*-valeric acid (3:8783), b.p. 222°.

3:5860 (1) Servais, *Rec. trav. chim.* 20, 46-47 (1901).

— 1,1,1-TRICHLOROPROPANOL-2



Beil I - (365)

I<sub>1</sub>-(185)

I<sub>2</sub>-(385)

B.P. 161.8° at 774 mm.

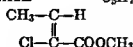
M.P. 50°

See 3:0846. Division A: Solids.

3:5870 METHYL  $\alpha$ -CHLOROCROTONATE

$\text{C}_5\text{H}_7\text{O}_2\text{Cl}$

Beil II - 414



II<sub>1</sub>-(189)

II<sub>2</sub>-(395)

B.P. 161-162°

(1)

$D_4^{23.7} = 1.1570$

(1)

161.5-161.7° at 762 mm. (2)

$D_4^{23.1} = 1.1575$

(1)

$n_D^{23.1} = 1.45689$  (1)

161° (3)

160.8° (4)

$D_4^{22.6} = 1.1587$

(2)

$n_D^{22.6} = 1.45634$  (2)

158-159° (5)

$D_4^{20} = 1.160$

(1)

59.0-59.5° at 16 mm. (5)

$D_4^{19} = 1.166$

(5)

$n_D^{19} = 1.455$  (5)

Note that the stereoisomeric methyl  $\alpha$ -chloroisocrotonate is unreported.

[For prepn. of  $\bar{C}$  from  $\alpha$ -chlorocrotonic acid (3:2760) in MeOH with HCl gas (65% yield (5)) (1) (4); from  $\alpha,\alpha,\beta$ -trichloro-*n*-butyraldehyde (butylchloral) (3:1905) (as hydrate) in MeOH below 15° with KCN (2 moles) (85% yield (3)); or from methyl  $\alpha$ -chloro- $\alpha$ -vinylacetate (5) by isomerization with NaOAc/AcOH on refluxing 30-40 hrs. (5) see indic. refs.]

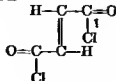
$\bar{C}$  is unaffected by AgOH (dif. from methyl  $\alpha$ -chloro- $\alpha$ -vinylacetate (5)).

3:5870 (1) von Auwers, *Ber.* 45, 2806 (1912). (2) Eisenlohr, *Ber.* 42, 3208 (1911). (3) Chattaway, Irving, *J. Chem. Soc.* 1929, 1045. (4) Kahlbaum, *Ber.* 12, 343-344 (1879). (5) Rambaud, *Bull. soc. chim.* (5) 1, 1353-1354 (1934).

3:5875 FUMARYL (DI)CHLORIDE

$\text{C}_4\text{H}_2\text{O}_2\text{Cl}_2$

Beil II - 743



II<sub>1</sub>-(302)

II<sub>2</sub>-(639)

B.P. 161-164°

(1)

$D_4^{20} = 1.408$

(3)

$n_D^{18.1} = 1.50038$  (3)

160° (2)

158-160° (3)

$D_4^{16.8} = 1.4117$

(3)

76° at 33 mm. (4)

59° at 16 mm. (5)

60° at 14 mm. (6)

62-64° at 13 mm. (7)

[For prepn. of  $\bar{C}$  from fumaric acid (1:0395) with  $\text{PCl}_5$  (1) (2) (3), with  $\text{SOCl}_2$  (8) (10) (cf. (9) (11)), with phthalyl dichloride (3:6900) (12) (9) (10), or with benzotrichloride (3:6540) at 170° (27) see indic. refs.; from maleic anhydride (1:0625) by htg. 2 hrs. at

130–135° with phthaloyl dichloride (3:6900) +  $\text{ZnCl}_2$  (82–95% yield (7)) or with  $\text{PCl}_5$  (13) (6) for formn. of  $\bar{C}$  from succinyl dichloride (3:6200) with  $\text{Cl}_2$  see (14), from calcium malate with  $\text{PCl}_5$  see (15).]

$\bar{C}$  on htg. with fumaric acid (1:0895) at 175° (9) (16) or with silver fumarate (13) is largely converted to maleic anhydride (1:0625), b.p. 197–199°, m.p. 52°.

$\bar{C}$  with  $\text{Cl}_2$  in  $\text{CCl}_4$  in sunlight adds halogen almost quant. (19) yielding (17) (18) (20) *meso*- $\alpha, \alpha'$ -dichlorosuccinyl dichloride (3:9087). —  $\bar{C}$  adds  $\text{Br}_2$  at 150° (2) or in  $\text{CCl}_4$  in sunlight (20) yielding alm. quant. (19) *meso*- $\alpha, \alpha'$ -dibromosuccinyl dichloride, h.p. 113° at 18 mm. (20) (this prod. hydrolyzes with aq. to *meso*- $\alpha, \alpha'$ -dibromosuccinic acid, m.p. 257–258° in s.t. (20)).

$\bar{C}$  with 1,4-diphenylbutadiene-1,3 yields (10) 3,6-diphenyltetrahydrophthaloyl dichloride, colorless ndls from lgr., m.p. 143–144° cor. (10), this prod. on long boilg. (7½ hrs.) with aq. alc. NaOH gives (10) on acidif. 3,6-diphenyltetrahydrophthalic acid, ndls. from AcOH, m.p. 230–231° cor. dec. (10).] — [For color reactns. of  $\bar{C}$  with various polyenes see (21).]

$\bar{C}$  on htg. at 100° with  $\text{AlCl}_3$  is partially conv. to maleyl dichloride accompanied by evolution of  $\text{HCl} + \text{CO}$  (22). —  $\bar{C}$  with  $\text{AlCl}_3 + \text{C}_6\text{H}_6$  gives (yield: 78–83% (23), 74% (24)) *trans*- $\alpha, \beta$ -dihenzoyl ethylene (1,4-diphenylbuten-2-dione-1,4), cryst. from  $\text{C}_6\text{H}_6$  by addn. of alc., pale yel. ndls., m.p. 109–110° (23).] [For corresp. reactn. of  $\bar{C} + \text{AlCl}_3$  with toluene (24) (25), chlorobenzene (24), mesitylene (24), anisole (24), *m*-xylene (25), and biphenyl (25) see indic. refs.]

$\bar{C}$  with excess MeOH yields (8) dimethyl fumarate (1:2415), m.p. 101.7°. (Note, however, that  $\bar{C}$  with 1 equiv. MeOH in  $\text{C}_6\text{H}_6$  stood 5 hrs. at room temp. (5) or in ether (26) yields fumaric methyl ester chloride, b.p. 83° nt 17 mm. (26), 76° at 22-mm. (5), m.p. 16° (5), this on shaking with aq. gives nlm. quant. (5) methyl hydrogen fumarate, cryst. from  $\text{C}_6\text{H}_6$ , m.p. 144.5° cor (5).

$\bar{C}$  with phenol (6) or with sodium phenolate in  $\text{C}_6\text{H}_6$  (28) yields diphenyl fumarate, ndls. from alc., m.p. 161–162° (6); note, however, that the hmf ester, phenyl hydrogen fumarate, has m.p. 130° (28).

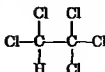
$\bar{C}$  with aq. readily hydrolyzes yielding fumaric acid (1:0895), m.p. nht. 293–295° subl.; for the diamide, dianilide, and other derivs. corresp. to  $\bar{C}$  see fumaric acid (1:0895).

3:5875 (1) Perkin, *J. Chem. Soc.* 53, 575 (1888). (2) Kekulé, *Ann. Suppl.* 2, 86–87 (1862/63). (3) von Auwers, Schmidt, *Ber.* 46, 480 (1913). (4) Wassermann, *Ann.* 488, 225 (1931). (5) Lutz, *J. Am. Chem. Soc.* 52, 3430 (1930). (6) Anschütz, Wirtz, *Ber.* 18, 1947–1949 (1885). (7) Kyrides, *Org. Syntheses*, 20, 51–54 (1940). (8) Meyer, *Monatsh.* 22, 421–422 (1901). (9) W. A. van Dorp, G. C. A. van Dorp, *Rec. trav. chim.* 25, 96–99 (1906). (10) Kuhn, Wagner-Jauregg, *Ber.* 63, 2664, 2678–2679 (1930).

(11) McMaster, Ahmann, *J. Am. Chem. Soc.* 50, 147 (1928). (12) Kyrides, *J. Am. Chem. Soc.* 59, 208 (1937). (13) Perkin, *Ber.* 14, 2545–2549 (1881). (14) Kauder, *J. prakt. Chem.* (2) 31, 24–25 (1885). (15) Perkin, Duppa, *Ann.* 112, 24–26 (1859). (16) G. C. A. van Dorp, P. J. Montagne, *Rec. trav. chim.* 37, 295 (1916). (17) Michael, Tissot, *J. prakt. Chem.* (2) 46, 394–395 (1892). (18) Holmberg, *J. prakt. Chem.* (2) 81, 148 (1911). (19) Lutz, *J. Am. Chem. Soc.* 49, 1109–1110 (1927). (20) Michael, *J. prakt. Chem.* (2) 52, 295 (1895).

(21) Kuhn, Wagner-Jauregg, *Helv. Chim. Acta* 13, 11 (1930). (22) Ott, *Ann.* 392, 272–273 (1912). (23) Lutz, *Org. Syntheses* 26, 29–32 (1940). (24) Conant, Lutz, *J. Am. Chem. Soc.* 45, 1303–1307 (1923). (25) Oddy, *J. Am. Chem. Soc.* 45, 2156–2160 (1923). (26) Anschütz, *Ann.* 461, 188–189 (1928). (27) Faber (to Turnbull), U.S. 1,793,917, Feb. 21, 1931; *Cent.* 1931, II 155. (28) Bischoff, von Hedenström, *Ber.* 35, 4056–4088 (1902).

3:5880 PENTACHLOROETHANE  
("Pentalin")

 $\text{C}_2\text{HCl}_5$ 

Beil. I - 87

I<sub>1</sub>-(26)I<sub>2</sub>-(57)

B.P.

F.P.

162.0°	at 760 mm. (1)	-29.5° (14)	$D_4^{25} = 1.67291$ (1)	
161.95°	at 760 mm. (2)	-29.0° (1)	1.6712 (13)	
	(3) (24)	(2) (15)		$n_D^{24} = 1.50250$ (6)
161.73°	(4)	-22° (16)		1.501 (17)
161-162°	(5)			
160.5°	(6)	See also	$D_4^{20} = 1.68052$ (1)	$n_D^{20} = 1.50348$ (80)
159.1° cor. at 760 mm.	(7)	Note 2. .		
159-160°	(8)		$D_4^{15} = 1.68813$ (1)	$n_D^{15} = 1.50542$ (1)
159-160° at 753 mm.	(9)		1.6846 (13)	
159°	(10)			
158.5-159.5°	(11)			
158°	at 760 mm. (12)			
157.8°	at 734 mm. (13)	Note 1. For additional data on vapor press. of $\bar{\text{C}}$ at 5° intervals from 15-165° see (18).		
152.2°	at 644 mm. (13)			
147.0°	at 563 mm. (13)			
149.8°	at 479 mm. (13)			
135.1°	at 406 mm. (13)	Note 2. For effect of press. on f.p. of $\bar{\text{C}}$ see (15).		
128.2°	at 327 mm. (13)			
119.0°	at 247 mm. (13)			
108.2°	at 172 mm. (13)			
93.6°	at 103 mm. (13)			
69.0°	at 37 mm. (13)			

See also Note 1.

Colorless liquid with odor suggesting chloroform. —  $\bar{\text{C}}$  is widely used in industry as solvent, degreasing agent, dry cleaner, component of insecticides, etc. — Note that comml.  $\bar{\text{C}}$  is likely to contain other prods., notably tetrachloroethylene (3:5460) q.v.

$\bar{\text{C}}$  is very spar. sol. aq.; e.g., 1 g.  $\bar{\text{C}}$  requires for soln. at 25° 2900 g. aq. (19); for study of soly. of  $\bar{\text{C}}$  in aq. at 20° see (20); for study of soly. of aq. in  $\bar{\text{C}}$  at 0°, 25°, and 30° as detd. by Karl Fischer reagt. see (21).

Binary systems contg.  $\bar{\text{C}}$ . For f.p./compn. data on systems  $\bar{\text{C}}$  + 1,2-dichloroethane (ethylene dichloride) (3:5130), eutectic, f.p. -62°, contg. about 56 wt. %  $\bar{\text{C}}$  (22);  $\bar{\text{C}}$  + 1,1,1-trichloroethane (methylchloroform) (3:5035), eutectic, f.p. -69.0° contg. 72.3%  $\bar{\text{C}}$  (14);  $\bar{\text{C}}$  + 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750), eutectic, f.p. -73°, contg. 59.9 wt. %  $\bar{\text{C}}$  (22);  $\bar{\text{C}}$  + tetrachloroethylene (3:5460), eutectic, f.p. -54.8°, contg. 41.6%  $\bar{\text{C}}$  (14);  $\bar{\text{C}}$  +  $\text{CCl}_4$  (3:5100), eutectic, f.p. -68° (82),  $\bar{\text{C}}$  +  $\text{CBr}_4$  (82) see indic. refs.

$\bar{\text{C}}$  forms binary azeotropes with various org. cpds.; e.g.,  $\bar{\text{C}}$  with chloroacetic acid (3:1370) forms a const.-boilg. mixt., b.p. 153.65° at 760 mm., contg. 90.1 wt. %  $\bar{\text{C}}$  (23);  $\bar{\text{C}}$  with trichloroacetic acid (3:1150) forms a const.-boilg. mixt., b.p. 161.8° at 760 mm., contg. 96.5 wt. %  $\bar{\text{C}}$  (24). — For other examples see Beil. I<sub>2</sub>-(57).

$\bar{\text{C}}$  either as liquid or vapor is extremely toxic; for further details see (83) (25) (26) (27) (28) (29); for extensive study of anthelmintic action see (19).

[For study of soly. in  $\bar{\text{C}}$  of gaseous  $\text{HCl}$  (30) (11),  $\text{H}_2\text{S}$  (30), or  $\text{NH}_3$  (30) see indic. refs.; for study of thermal conductivity of  $\bar{\text{C}}$  see (31); for study of influence of vapors of  $\bar{\text{C}}$  on

the explosion limits of mixtures of air with hydrogen, carbon monoxide, methane, acetylene, etc., see (32) (33) (34) (35).]

Preparation of  $\bar{C}$ . [For prepn. of  $\bar{C}$  from chloral (3:5210) with  $PCl_5$  (7) (37) or with  $AlCl_3$  (38) see indic. refs.; note that in latter case (38) presence of  $AlCl_3$  also facilitates loss of  $HCl$  from  $\bar{C}$  with consequent formn. of tetrachloroethylene (3:5460); from trichloroethylene (3:5170) by addn. of  $Cl_2$  in aq. (39) or under influence of ultra-violet light (40) (41) (note that  $O_2$  retards addition of halogen (41)), or with  $S_2Cl_2$  in s.t. at 140–150° (42), see indic. refs.]

[For formn. of  $\bar{C}$  (together with various other by-products) from ethyl chloride (3:7015) (43) or from 1,2-dichloroethane (ethylene dichloride) (3:5130) (44) with  $Cl_2$  see indic. refs.; from chloroform (3:5050) in electric arc (45) or in dark electric discharge (46) see indic. refs.; from  $CCl_4$  in dark elec. discharge see (46); from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) or from trichloroethylene (3:5170) with  $Cl_2$  at 80°, 95°, or 115° in ultra-violet light (41), over pumice at 700° (47), or with  $FeCl_3$  on htg. in s.t. (48) see indic. refs.; from trichloroethylene (3:5170) with large excess  $Cl_2O$  in  $CCl_4$  at –20° see (10); from  $\beta,\beta'$ -dichlorodiethyl sulfide ("mustard gas") with dry  $Cl_2$  at 100° see (49).]

[For stabilization of  $\bar{C}$  by addn. of not over 0.1% alkyl amines such as  $Et_3N$  (50) or with a wide variety of other org. N cpds. (81) see indic. refs.]

[For studies of detn. of  $\bar{C}$  by reactn. with  $Na$  + ethanalamine in dioxane (51) followed by volumetric (51) or gravimetric (71) detn. of resultant chloride ion see indic. refs. (note that use of Stepanov's method ( $Na$  +  $EtOH$ ) for detn. of  $Cl$  in  $\bar{C}$  gives low results unless after addn. of  $Na$  mixt. is refluxed at least 20 hrs. (12)); for detn. of  $\bar{C}$  by thermal decn. and subsequent detn. of chlorine see (52).]

Chemical behavior of  $\bar{C}$ . [ $\bar{C}$  with dry  $Cl_2$  at 70° in diffuse light does not react and even after 30 hrs. no  $HCl$  is formed (52); however,  $\bar{C}$  with dry  $Cl_2$  +  $AlCl_3$  at 70° (53), or  $\bar{C}$  +  $Cl_2$  over activated charcoal at 300–400° (54), yields hexachloroethane (3:4835).]

[ $\bar{C}$  with  $F_2$  at 90° over a 10-hr. period yields (8) a mixt. of prods. contg. fluoropentachloroethane, m.p. 99.8–110° (in s.t.) (b.p. 137–139°), hexachloroethane (3:4835), tetrachloroethylene (3:5460), *sym.*-difluorotetrachloroethane, b.p. 91–92°, together with other materials. — For behavior of  $\bar{C}$  with  $SbF_5$  see (55).]

$\bar{C}$  with  $K_2Cr_2O_7/H_2SO_4$  is only partially oxidized to  $CO_2$  (56). — [ $\bar{C}$  on photochem. oxidn. with  $O_2$  in ultra-violet light (57) (58) gives a mixt. consisting of 80% trichloroacetyl chloride (3:5420) + 20% phosgene (3:5000). —  $\bar{C}$  with fuming  $H_2SO_4$  (60%  $SO_3$ ) at 50–60° yields (59) dichloroacetyl chloride (3:5200).]

$\bar{C}$  under various circumstances loses  $HCl$  yielding tetrachloroethylene (3:5460) [e.g.,  $\bar{C}$  over bone char at 280° (60) or over  $NiCl_2$  at 330° (61), or with  $AlCl_3$  at 70° (53) or under reflux (95% yield (72)) (62), or with liq.  $NH_3$  at –18 to –34° under reduced press. (63) (64), or with prim. or sec. aliph. amines (84), or with  $MeOH$  over  $Al_2O_3$  at 290° (methyl chloride (3:7005) is also formed) (65), or with acetylene over cat. at 200–300° (vinyl chloride (3:7010) is also formed) (68), or with alc.  $KOH$  (44) (66), or in alc. with 2  $N$  aqueous  $NaOH$  in cold (98% yield (12)) gives tetrachloroethylene (3:5460). — For detn. of  $\bar{C}$  by titration of chloride ion thus split off see (67); for study of kinetics of reactn. of  $\bar{C}$  with  $EtOH/NaOH$  see (12).]

$\bar{C}$  under certain conditions yields trichloroethylene (3:5170) [e.g.,  $\bar{C}$  with  $H_2$  over  $Ni$  at 270° (61), or  $\bar{C}$  on electrolysis at  $Pb$  cathode (69), or  $\bar{C}$  with  $MeMgI$  (70) gives trichloroethylene (3:5170).]

[ $\bar{C}$  with  $CHCl_3$  (3:5050) +  $AlCl_3$  gives (72) (73) (74) (75) *unsym.*-heptachloropropane (3:0200); note that this reactn. first involves loss of  $HCl$  under influence of  $AlCl_3$  (see also above) and subsequent condensation of the resultant tetrachloroethylene (3:5460)

with  $\text{CHCl}_3$ . —  $\bar{\text{C}}$  (1 mole) + 1,2-dichloroethylene (presumably mixt. of *cis* (3:5042) and *trans* (3:5028) stereoisomers) +  $\text{AlCl}_3$  (1% of sum of wts. of reactants) stood 12 days at  $40^\circ$  gives (76) (in addition to a residue a fraction volatile with steam which consists of 1,1,2,2,3,4,4-heptachlorobutane (3:0056)), two stereoisomeric 1,1,2,3,4-pentachlorobutanes, viz., the solid isomer (3:0750) and the liquid isomer (3:9068); for genesis of these compds. see (76).]

[For survey of actn. of  $\bar{\text{C}}$  on various common metals see (77). —  $\bar{\text{C}}$  with Na or K or their alloys may (like many other polychloro compds.) explode under certain conditions; for an extensive study of this behavior including sensitivity to mechanical shock see (78).]

$\bar{\text{C}}$  with excess phenylhydrazine on stdg. at ord. temp. evolves  $\text{N}_2$ , ppts. phenylhydrazine hydrochloride, and yields benzene (67); the full mechanism of this behavior seems never to have been established, but these same three prods. are similarly obtd. from hexachloroethane (3:4835) and to a lesser degree from 1,1,2,2-tetrachloroethane (3:5750).

⑤ Color test with  $\text{NH}_4\text{OH}/\text{Cu}_2\text{Cl}_2$ .  $\bar{\text{C}}$  (1-2 drops) in small glass-stoppered bottle filled with conc. aq.  $\text{NH}_4\text{OH}$  treated with powdered  $\text{Cu}_2\text{Cl}_2$ , stopper quickly inserted (to force out air and excess liq.) and shaken, gives within 5 mins. a blue color which rapidly darkens; note that this test is not specific for  $\bar{\text{C}}$  and is also shown by other epds. contg. the  $-\text{CCl}_3$  group such as trichloroacetic acid (3:1150), ethyl trichloroacetate (3:5950)  $\text{CHCl}_3$  (3:5050),  $\text{CCl}_4$  (3:5100), although hexachloroethane (3:4835) develops color at surface only after several hours; for further details see (79).

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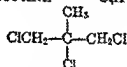
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### 3:5885 1,2,3-TRICHLORO-2-METHYLPROPANE $C_4H_7Cl_3$ Beil. S.N. 10



B.P. 162.0-163.1° cor. (1)

$D_4^{25} = 1.3020$  (1)

$n_D^{20} = 1.4765$  (1)

{For prepn. of  $\bar{C}$  from *ter*-butyl chloride (3:7045) +  $\text{Cl}_2$  see (1); for formn. of  $\bar{C}$  (5%) from 3-chloro-2-methylpropene-1 (methallyl chloride) (3:7145) by addn. of  $\text{Cl}_2$  with  $\text{Cl}_2/\text{aq.}$  at 30° (main prod. is 1,3-dichloropropanol-2 (3:5985) in 70% yield) (2), or better with  $\text{SO}_2\text{Cl}_2$  (83% yield (4)) see indic. refs.; from 1,3-dichloro-2-methylpropene (3:7960) with  $\text{Cl}_2$ , or with  $\text{SO}_2\text{Cl}_2 + \text{Bz}_2\text{O}_2$  (73% yield) see (4).}

$\bar{C}$  on pyrolysis at 450-550° gives (3) three isomeric dichloroisobutenes, viz., *cis* and *trans* 1,3-dichloro-2-methylpropene (3:5590) and 3-chloro-2-(chloromethyl)propene-1 (3:5633).

[ $\bar{C}$  on dehydrohalogenation with equimolar proportion of quinoline at b.p. 1½ hrs. gives (73-83% yield (4)) 1,3-dichloro-2-methylpropene-1 (3:5590).]

$\bar{C}$  on hydrolysis with excess 5% aq. NaOH gives (84% yield (3)) a mixt. of *cis* and *trans* stereoisomers of  $\gamma$ -chloro- $\beta$ -methyl-allyl alcohol (3:8340).

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3:5800 ISOPROPYL DICHLOROACETATE  $C_5H_8O_2Cl_2$  B.  
 $(CH_3)_2CH.O.CO.CHCl_2$

B.P. 163.8-164.8° (1)  $D_4^{25} = 1.1989$  (2)  $n_D^{25} =$   
 164.0° at 747 mm. (2)  $D_4^{20} = 1.2053$  (3)  $n_D^{20} =$

[For prepn. (48.6% yield (2)) from isopropyl alc. (1:6135) + dichloroacetic ac. see (2); for prepn. (39.5% yield (2)) from propylene and dichloroacetic ac. (3: (2).]

[For study of hydrolysis of  $\bar{C}$  see (3).]

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3:5895 1,2,2,3-TETRACHLOROPROPANE  $C_3H_4Cl_4$  Beil.  
 $Cl.CH_2-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2Cl$  1  
 1

B.P. 164° (1)  $D_{17}^{17} = 1.496$  (1)

Colorless liq. with characteristic penetrating ethereal odor. — Insol. in aq.; en alc., ether.

[For prepn. of  $\bar{C}$  from 2,3-dichloropropene-1 (3:5190) with  $Cl_2$  see (1); from 1,2-chloropropane (3:5475) with  $SbCl_5$  at 100° see (2).]

$\bar{C}$  with alc. KOH splits out HCl yielding (1) 1,2,3-trichloropropene-1 (3:5650), b.p.

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3:5900 1,3-DICHLOROBUTANONE-2  $C_4H_6OCl_2$  Beil. I - 6;  
 ( $\alpha$ -Chloroethyl chloro-  $Cl.CH_2.CO-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$  I<sub>1</sub>-(3)  
 methyl ketone) I<sub>2</sub>—

B.P. 165° (2) at 753 mm. (1)  $D_4^{20} = 1.3116$  (3)  $n_D^{20} = 1.4686$  (4)  
 65° at 17 mm. (2)  $D_4^{15} = 1.3189$  (3)  $n_D^{15} = 1.4702$  (4)  
 60° at 13 mm. (2)  
 55-55.5° at 10 mm. (3)

Colorless liq. when freshly distd. but gradually turns red. — Strong lachrymator and nasal irritant (1). — Insol. aq.; sol. alc., ether, and most org. solvents.

[For prepn. from ethyl methyl ketone (1:5405) by actn. of  $Cl_2$  (1), from 1,3-dichlorobutanol-2 (3:9145) by oxidn. (3); from 3-chloro-2-(chloromethyl)butene-1 (3:9206) with  $O_3$  (4) see indic. refs.]

$\bar{C}$  with satd. aq.  $NaHSO_3$  soln. yields cryst.  $NaHSO_3$  cpd. (1). —  $\bar{C}$  with Zn dust + AcOH yields (1) (3) ethyl methyl ketone (1:5405).

① 1,3-Dichlorobutanone-2 semicarbazone: m.p. 114° (2), 107-108° (4).

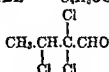
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3:5916  $\alpha, \alpha, \beta$ -TRICHLORO-*n*-BUTYRALDEHYDE  
 ("Butyrychloral"; "Butylchloral";  
 Crotonchloral)

 $C_4H_5OCl_3$ 

Beil. I - 664

 $I_1$ -(340)

 $I_2$ -(725)


B.P.

164.5-165.5° at 760 mm. (1)

 $D_4^{20} = 1.3956$  (4)  $n_D^{20} = 1.47554$  (4)

165° (2)

164-165° at 750 mm. (3) (4)

 $D_{15}^{18} = 1.4237$  (5)

163-164° (6)

[See also "Butyrychloral hydrate" (3:1905).]

Oily liq.

[For prepn. of  $\bar{C}$  from acetaldehyde (1:6100) (3) (7) or paraldehyde (1:0170) (7) (8) with  $Cl_2$  see indic. refs.; from  $\alpha$ -chlorocrotonaldehyde (3:8117) by addn. of  $Cl_2$  (6) (10) (36) in  $CCl_4$  soln. (9); from crotonaldehyde (1:6150) by satn. with  $HCl$  gas followed by treatment with  $Cl_2$  see (11) cf. (37).]

[For prepn. of  $\bar{C}$  from its polymers (see below) by distn. at atmospheric press. (2), or from its hydrate (3:1905) by distn. with half its wt. of  $Ac_2O$  (2), or shaking with conc.  $H_2SO_4$  (1) cf. (2), see indic. refs.]

[ $\bar{C}$  on reduction with fused  $Al(OEt)_3$  in boilg. abs. alc. under  $H_2$  or  $N_2$  for 14 hrs. (12) or with fused  $Al(OEt)_3 + AlCl_3$  in boilg. abs. alc. under  $H_2$  or  $N_2$  for 14 hrs. (13), or with  $C_2H_5OMgBr$  in dry ether followed by aq. (19), or by treatment with diethylzinc (14), di-*n*-propylzinc (15), or di-isobutylzinc (15) (followed by aq.) gives (92% yield (12)) 2,2,3-trichlorobutanol-1 (3:1336), m.p. 62°. — Note that  $\bar{C}$  (as hydrate) (3:1905) is reduced by fermenting yeast (16) to dextrorotatory 2,2,3-trichlorobutanol-1, m.p. 62°.]

[ $\bar{C}$  with  $Zn + HCl$  or  $Zn + aq.$  (17) is dehalogenated to a mixt. of  $\alpha$ -chlorocrotonaldehyde (3:8117) + crotonaldehyde (1:0150);  $\bar{C}$  with  $Fe$  filings +  $AcOH$  at room temp. for 8 days (18) dehalogenates to a mixt. of *n*-butyraldehyde (1:0130) + *n*-butyl alc. (1:6180) + crotonyl alc. (Beil. I-442,  $I_1$ -(227),  $I_2$ -(480)).]

$\bar{C}$  on oxidn. with 2 pts. fung.  $HNO_3$  stood overnight at ord. temp. yields (3)  $\alpha, \alpha, \beta$ -trichloro-*n*-butyric acid (3:1280) (cf. corresp. behavior of butyrychloral hydrate (3:1905)). —  $\bar{C}$  on oxidn. with boilg. aq.  $K_4Fe(CN)_6$  also loses 2 atoms of chlorine giving (41% yield (29))  $\alpha$ -chlorocrotonic acid (3:2760).

$\bar{C}$  (1 mole) with  $H_2O$  (1 mole) readily combines with evolution of heat yielding (3) (9) crystn. butyrychloral hydrate (3:1905). — Similarly,  $\bar{C}$  combines with equiv. amt. of alcohols giving the corresp. alcoholates: e.g.,  $\bar{C}$  with  $EtOH$  yields (20) butyrychloral-ethylalcoholate [Beil. I-665,  $I_1$ -(346)];  $\bar{C}$  with butanol-2 yields (1) butyrychloral-sec-butylalcoholate, etc. — Note that butyrychloral-ethylalcoholate in excess  $EtOH$  on satn. with dry  $HCl$  gas gives (50% yield (21))  $\alpha, \alpha, \beta$ -trichloro-*n*-butyraldehyde diethylacetal, b.p. 232-233°, 135° at 30 mm. (21). — [For study of dissociation of addn. epds. of  $\bar{C}$  with various *prim.*, *sec.*, and *ter.* alcohols see (22).]

$\bar{C}$  or its hydrate (3:1905) q.v. in pres. of conc.  $H_2SO_4$  or pyridine at ord. temp. can be trimerized to a mixt. of two parabutyrychlorals (2); these are colorless, crystalline, sharp melting solids, sol. in org. solvents but insol. in aq.; the less sol.  $\alpha$ -parabutyrychloral, rhombic cryst. from boilg.  $AcOH$  or boilg.  $EtOH$ , has m.p. 180°; the more soluble  $\beta$ -parabutyrychloral (stereoisomer?), cryst. from boilg.  $AcOH$  or boilg.  $EtOH$ , has m.p. 157°; these polymers can be distilled at 15 mm., but attempts to distil them at ord. press. result in complete dissociation to  $\bar{C}$  (2).

[ $\bar{C}$  with anhydrous acetaldehyde (1:0100) (2 moles) with dry HCl gas at 0° for 15-20 hrs. condenses to give (67% yield (23)) 2,4-dimethyl-6-( $\alpha,\alpha,\beta$ -trichloro-*n*-propyl)trioxane-1,3,5, h.p. 118° at 13 mm. (23).]

[ $\bar{C}$  in  $\text{CHCl}_3$  with  $\text{H}_2\text{S}$  gives (24) *bis*-( $\alpha$ -hydroxy- $\beta,\beta,\gamma$ -trichloro-*n*-butyl)sulfide ("butyrchloralsulphydrate"), m.p. 85° (24).]

[ $\bar{C}$  with  $\text{PCl}_5$  (1.4 wt. pts.) at 110-120° apparently has its oxygen replaced by equivalent chlorine but also loses 1 HCl yielding (25) a cpd. of compn.  $\text{C}_4\text{H}_2\text{Cl}_4$ , presumably 1,1,2,3-tetrachlorobutene-2, although no other report of this cpd. can be found.]

[ $\bar{C}$  with aq. HCN gives only butyrchloral hydrate (3:1905) since this prod. is too spar. sol. aq. to enter further reaction, but upon addn. of alc. and subsequent digestion this system yields (26) (27)  $\alpha,\alpha,\beta$ -trichloro-*n*-butyraldehyde cyanohydrin [Beil. 111-322, III- (226)], pl. from aq., m.p. 101-102° (27) (28), also obtd. from butyrchloral hydrate with aq. KCN (2 moles) at 40° (28). — See also further comments under butyrchloral hydrate (3:1905).]

[ $\bar{C}$  with ethyl diazoacetate gives (71% yield (30)) ethyl  $\beta$ -keto- $\gamma,\gamma$ -trichloro-*n*-caproate [Beil. III-684], b.p. 149° at 20 mm. (30).]

$\bar{C}$  in  $\text{CHCl}_3$  with  $\text{NH}_3$  gas gives on evapn. of solvent (31) butyrchloralammonia, cryst., m.p. 62° [see also under butyrchloral hydrate (3:1905)].

$\bar{C}$  also readily adds amides yielding cpds. of type  $\text{CH}_3\text{CHClCH}_2\text{CH}(\text{OH})\text{NH}\cdot\text{CO}\cdot\text{R}$ ; e.g.,  $\bar{C}$  with acetamide (1 mole) gives on htg. (31) (32) (33) (34) butyrchloralacetamide, obtd. by these workers in two isomeric forms one of m.p. 170° (spar. sol. hot alc.) (32) (33) (34), the other m.p. 158° (readily sol. in hot 50% alc.) (31) (32) (33); note, however, that butyrchloral hydrate (3:1905) with acetamide (1 mole) htd. at 100° until solidification occurs gives only (21) a prod. m.p. 208-210°;  $\bar{C}$  with benzamide (1 mole) gives on htg. butyrchloralbenzamide, obtd. in two isomeric forms, one of m.p. 146° (32) (33) cf. (34), the other of m.p. 132° (31) (32) (33); note, however, that butyrchloral hydrate (3:1905) with benzamids yields only (21) a prod. m.p. 176°.

$\bar{C}$  (3.5 g.) with urea (1.2 g.) htd. at 100°, cooled, powdered and recrystd. from alc., gives (yield not stated (35)) butyrchloralurea, m.p. 156°.

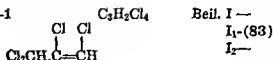
3:5910 (1) Willcox, Brunel, *J. Am. Chem. Soc.* 38, 1837 (1916). (2) Chattaway, Kellett, *J. Chem. Soc.* 1928, 2709-2714. (3) Krämer, Pinner, *Ber.* 3, 383-390 (1870). (4) Brühl, *Ann.* 203, 20 (1880). (5) Dobrosserdow, *Cent.* 1911, 1 955. (6) Pinner, *Ber.* 8, 1564-1566 (1875). (7) Pinner, *Ann.* 179, 24-30 (1875). (8) Freundler, *Bull. soc. chim.* (4) 1, 68-69 (1907). (9) Moureu, Murat, Tampier, *Bull. soc. chim.* (4) 29, 33 (1921). (10) Lieben, Zeisel, *Monatsh.* 4, 533-536 (1883).

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(21) Freundler, *Bull. soc. chim.* (4) 1, 201, 203-204 (1907); *Compt. rend.* 143, 684 (1906). (22) Willcox, Brunel, *J. Am. Chem. Soc.* 38, 2533-2535 (1916). (23) Helferich, Besler, *Ber.* 57, 1277, 1279-1280 (1924). (24) Voswinkel, *Ger.* 233,857, April 24, 1911; *Cent.* 1911, I 1467. (25) Judson, *Ber.* 3, 790 (1870). (26) Pinner, Bischoff, *Ann.* 179, 97-99 (1875). (27) Pinner, Klein, *Ber.* 11, 1488 (1878). (28) Chattaway, Irving, *J. Chem. Soc.* 1929, 1043-1046. (29) Wallach, *Ber.* 10, 1530 (1877). (30) Schlotterbeck, *Ber.* 42, 2572 (1909).

(31) Schiff, Tassinari, *Ber.* 10, 1784-1786 (1877). (32) Schiff, *Ber.* 25, 1690-1691 (1892). (33) Tarugi, *Gazz. chim. ital.* 24, I 230-236 (1894). (34) Pinner, *Ann.* 179, 39-40 (1875). (35) Feist, Kublinski, *Arch. Pharm.* 274, 430, 434 (1936). (36) Chem. Fabrik vorm. Weiler ter Meer, *Ger.* 351,137, April 3, 1922; *Cent.* 1922, IV 155. (37) Brown, Plump (to Pennsylvania Salt Mfg. Co.), U.S. 2,351,000, June 13, 1944; C.A. 38, 5226 (1944).

## 3:5920 1,2,3,3-TETRACHLOROPROPENE-1



B.P. 165° (1)  
165-167° (2)

$D_4^{24} = 1.5274$  (1)       $n_D^{18} = 1.5272$  (1)

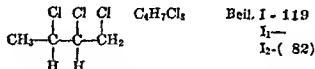
Colorless oil.

[For prepn. (70% yield (2)) from *sym*-pentachloropropane (3:5280) by actn. of alc. KOH (1 mole) see (2).]

$\bar{\text{C}}$  with conc.  $\text{H}_2\text{SO}_4$  at 30-40° gives quant. yield of chloromalondialdehyde [Beil. I-765].

3:5920 (1) Prins, *J. prakt. Chem.* (2) 89, 421-422 (1914). (2) Heilbron, Heslop, Irving, *J. Chem. Soc.* 1936, 783.

## 3:5935 1,2,3-TRICHLOROBUTANE



B.P. 165-167° at 759 mm. (1)  
165-168° at 725 mm. (2)  
79-80° at 32 mm. (3)  
62-63° at 28 mm. (2)

$D_4^{20} = 1.3164$  (1)       $n_D^{20} = 1.4799$  (1)

$D_4^{18} = 1.3172$  (1)  
 $D_0^0 = 1.3241$  (3)

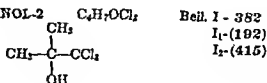
Insol. aq., sol. alc., ether,  $\text{CHCl}_3$ .

[For formn. of  $\bar{\text{C}}$  (36.5%) from 2,3-dichlorobutane (3:7615) + sl. excess  $\text{Cl}_2$  in dark at -17° (together with 18% 2,2,3-trichlorobutane (3:5680)) see (1); for formn. of  $\bar{\text{C}}$  (19%) from 1,2-dichlorobutane (3:7680) + sl. excess  $\text{Cl}_2$  in dark at -17° (together with 28% 2,2,3-trichlorobutane (3:5680)) see (1); for formn. of  $\bar{\text{C}}$  from 1-chlorobutene-2 (3:7205) +  $\text{Cl}_2$  in  $\text{CHCl}_3$  see (3); for formn. of  $\bar{\text{C}}$  from butene-1 with  $\text{Cl}_2$ /aq. (together with 1,2-dichlorobutane (3:7680)) see (2).]

$\bar{\text{C}}$  with solid KOH at 150° loses HCl yielding (1) mixt. of *cis*-1,2-dichlorobutene-2 (3:5615), b.p. 125-127°, and *trans*-1,2-dichlorobutene-2 (3:5360), h.p. 116-118° at 765 mm. (1).

3:5935 (1) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 6, 1553-1558 (1936); *C.A.* 31, 2165 (1937), *Cent.* 1937, 1 3786. (2) de Montmollin, Matile, *Helv. Chim. Acta* 7, 108 (1924). (3) Charon, *Ann. chim.* (7) 17, 230-231 (1899).

## — 1,1,1-TRICHLORO-2-METHYLPROPANOL-2



B.P. 167°

M.P. 96-97°

See 3:2662. Division A: Solids.

## 3:5956 ETHYL TRICHLOROACETATE



Beil. II - 209

II<sub>1</sub>-(94)II<sub>2</sub>-(200)

B.P. 167.5-168.0° cor.	(1)	$D_4^{20} = 1.3826$ (8)	$n_D^{20} = 1.45668$ (8)
167.5°	(2)	1.3823 (10)	1.45046 (10)
166.7-167.1° at 754.8 mm.	(3)		
167°	(4)		
166°	(13)		
166° at 738.2 mm.	(8)		
164-166°	(5)		
164°	(6)		
163.0-163.5° at 882 mm.	(7)		
74° at 28 mm.	(9)		
58.6-59.0° at 13 mm.	(10)		
62° at 12 mm.	(11)		
60-61° at 13 mm.	(12)		

[For prepn. of  $\bar{\text{C}}$  from trichloroacetic acid (3:1150) with abs. EtOH + dry HCl (yield: 90% (13), 53% (16)) or with  $\text{H}_2\text{SO}_4$  (50-60% yield (13)) (14) (15), or with Twitchell's reagt. (62.6% yield (5)) see indic. refs.; from trichloroacetyl chloride (3:5420) with ethyl orthoformate (1:3241) see (17); from "tetrachloroethylidene trichloroacetate" [Beil. XIX-105] with EtOH see (12); for formn. of  $\bar{\text{C}}$  from chloral (3:5210) with  $\text{Al}(\text{OEt})_3$  in  $\text{C}_6\text{H}_6$  (11), or with acetaldehyde +  $\text{Al}(\text{OEt})_3$  or  $\text{Mg}(\text{OMe})_2$  in dry ether (18), see indic. refs.]

[ $\bar{\text{C}}$  on warming with KCN in abs. alc. dec. (9) into chloroform (3:5050) +  $\text{CO}_2$ ;  $\bar{\text{C}}$  with NaOEt gives on warming (19) triethyl orthoformate (1:3241) + Na ethyl carbonate + NaCl.]

[ $\bar{\text{C}}$  with excess  $\text{H}_2$  over Ni at 320° gives (14) ethyl dichloroacetate (3:5850) + ethyl chloroacetate (3:5700) + EtOAc (1:3015) + acetaldehyde (1:0100).]

$\bar{\text{C}}$  with  $\text{Cu}_2\text{Cl}_2$  in conc. aq.  $\text{NH}_4\text{OH}$  gives dark blue color within 2 min. (21); also shown by chloral hydrate (3:1270) and trichloroacetic acid (3:1150) (the latter, however, acting instantly); for further limitations see (21). [ $\bar{\text{C}}$  htd. at 100° with Cu powder for 6-8 hrs. (22) gives diethyl tetrachlorosuccinate, b.p. 150° at 13 mm. (22).]

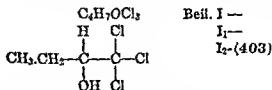
$\bar{\text{C}}$  with conc. aq.  $\text{NH}_4\text{OH}$  gives in the cold (14) trichloroacetamide, spar. sol. aq., cryst. from hot aq. or dil. alc., m.p. 141°. —  $\bar{\text{C}}$  on shaking with aq. benzylamine gives in the cold (23) trichloroacet-N-benzylamide, cryst. from lgr., m.p. 93.6-94.4° cor. (23). [Note, however, that the corresp. dichloroacet-N-benzylamide (from ethyl dichloroacetate (3:5850) has almost the same m.p., viz., 94.8-95.6° cor. (23), while chloroacet-N-benzylamide (from ethyl chloroacetate (3:5700)) has m.p. 93.0-93.6° cor. (23).]

$\bar{\text{C}}$  hydrolyzes very readily (5) yielding ethyl alcohol (1:0130) and trichloroacetic acid (3:1150). [For kinetic studies of hydrolysis of  $\bar{\text{C}}$  under various conditions (including very high pressure (9)) see (10) (2) (24); for kinetic study of alcoholysis of  $\bar{\text{C}}$  with MeOH + HCl see (25).]

- 3:5950 (1) Perkin, *J. Chem. Soc.* 65, 423 (1891). (2) Timm, Hinshelwood, *J. Chem. Soc.* 1938, 802-809. (3) Schiff, *Ann.* 220, 198 (1893); *Z. physik. Chem.* 1, 379 (1887). (4) Cheng, *Z. physik. Chem.* B-24, 306 (1934). [(5) Zaganianis, Varvogles, *Ber.* 69, 2289 (1936). (6) Claus, *Ann.* 191, 58-63 (1878). (7) Sudborough, Karne, *J. Indian Inst. Sci.* 5, 7 (1922); *Cent.* 1923, I 295; C.A. 17, 665 (1923). (8) Brühl, *Ann.* 203, 22-23 (1880). (9) Newitt, Linstead, Sapiro, Boorman, *J. Chem. Soc.* 1937, 876-883. (10) Palomaa, Salmi, Korte, *Ber.* 72, 790-797 (1939). (11) Dworzak, *Monatsh.* 47, 11-15 (1920). (12) Anschütz, Haslam, *Ann.* 253, 125 (1889). (13) L. Spiegel, P. Spiegel, *Ber.* 40, 1734 (1907). (14) Clermont, *Compt. rend.* 133, 737-738

- (1901). {15} Dumas, *Ann.* 32, 112 (1839). {16} Toole, Sowa, *J. Am. Chem. Soc.* 59, 1972 (1937).  
 {17} Levailant, *Compt. rend.* 195, 882 (1932). {18} Nakai, *Biochem. Z.* 152, 269-273 (1924).  
 {19} Sabatier, Mailhe, *Compt. rend.* 169, 760 (1919).  
 {20} Doughty, Freeman, *J. Am. Chem. Soc.* 59, 421-422 (1937).  
 {21} Jackenzie, *J. Am. Chem. Soc.* 59, 421-422 (1937).  
 {22} Kolhatkar, *J. Chem. Soc.* 107, 930 (1915).

**3:5955 *d,l*-1,1,1-TRICHLOROBUTANOL-2**  
 (Ethyl-trichloromethyl-carbinol)



B P. 169-171° at 738 mm. {1}  
 82-84° at 22 mm. {2}  
 69-71° at 12 mm. {3}  
 68-70° at 13 mm. {1}  
 44-46° at 3 mm. {1}

$D_{25}^{25} = 1.3760$  {1}  $n_D^{25} = 1.4901$  {1}

Oil. — Eas. sol. MeOH, EtOH, ether, acetone,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CS}_2$ . [Note that b.p. of 99° at 680 mm. {1} may be a typographical error {1}.]

[For prepn. of  $\bar{\text{C}}$  from chloral (3:5210) via conversion with diazomethane to 3,3,3-trichloro-1,2-epoxypropane (3:1336) and reactn. of latter with 1 N LiMe in dry ether at -75° (yield 85%) see {1}; from chloral (3:5210) with  $\text{EtMgBr}$  {4} {5} or  $\text{EtMgI}$  {2} in ether (yields: 44% {4}, 16% {2}, 15% {5}) see indic. refs. (note, however, that by virtue of reducing actn. of  $\text{EtMgX}$  large amounts of 2,2,2-trichloroethanol-1 (3:5775) are also formed {5} {2} {1}); from chloral (3:5210) with  $\text{PbEt}_4$  (20% yield {6}) (note, however, that this could not be confirmed {1}), from trichloroacetyl chloride (3:5420) with  $\text{EtMgBr}$  at 10° see {3}.]

$\bar{\text{C}}$  with conc.  $\text{HCl} + \text{ZnCl}_2$  (Lucas' reagent) stood for 1 hr. at room temp. gives {1} 1,1,1,2-tetrachlorobutane (3:5622).

$\bar{\text{C}}$  with 5% soln. of  $\text{Na}_2\text{CO}_3$  in 50% aq. alc. refluxed for 10 hrs. {1} or  $\bar{\text{C}}$  with aq.  $\text{KOH}$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{CaCO}_3$ , etc., {2} undergoes both hydrolysis and hydrolytic cleavage giving respectively  $\alpha$ -hydroxy-*n*-butyric acid [Beil. III-302, III<sub>1</sub>-(114), III<sub>2</sub>-(216)] (yields: 46% {1}, 21% {2}), m.p. 43°, and propionaldehyde (1:0110) (29% yield {2}).

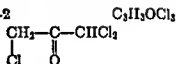
— Ethyl-trichloromethyl-carbinyl acetate: b.p. 164-165° at 680 mm. {4}. [From  $\bar{\text{C}}$  with  $\text{Ac}_2\text{O}$  at 130-135° for 2 hrs. {4}. Note that in light of subsequent work {1} the identity of this prod. has been questioned.]

— Ethyl-trimethyl-carbinyl benzoate: b.p. 217-218° at 680 mm. {4}. [From  $\bar{\text{C}}$  with  $\text{BzCl} +$  cold dil. aq. alk. {4}. Note that in light of subsequent work {1} the identity of this prod. has been questioned.]

Ⓔ Ethyl-trimethyl-carbinyl *p*-nitrobenzoate: cryst. from pet. ether, m.p. 70-71.5° {1}. [Note that this m.p. is identical with that of the *p*-nitrobenzoate of 2,2,2-trichloroethanol-1 (3:5775); although each appears to be authentic, whether their mixture shows depression of m.p. is not reported.]

3:5955 {1} Gilman, Abbott, *J. Org. Chem.* 8, 224-229 (1943). {2} Hébert, *Bull. soc. chim.* {4} 27, 49, 55 (1920). {3} Jacob, *Bull. soc. chim.* {5} 7, 581-586 (1940); *C.A.* 36, 3507 (1942). {4} Howard, *J. Am. Chem. Soc.* 48, 774-775 (1926). {5} Iotsich, *J. Russ. Phys.-Chem. Soc.* 36, 415 (1904); *Bull. soc. chim.* {3} 34, 329 (1905). {6} Meerwein, Hinz, Majert, Sönke, *J. prakt. Chem.* {2} 147, 234, Note 1 (1936).

## 3:5957 1,1,3-TRICHLOROPROPANONE-2

 $(\alpha, \alpha, \gamma\text{-Trichloroacetone})$ 

Bell. I - 655

I<sub>1</sub>—I<sub>2</sub>—

B.P. 172° (1)

[For prepn. of  $\bar{C}$  from 1,1-dichloro-3-bromopropanone-2 (1) with alc.  $\text{HgCl}_2$  see (1); for formn. from acetone (1:5400) with  $\text{Cl}_2$  in pres. of  $\text{NiCl}_2$  at 70° (together with other prods.) see (2).]

$\bar{C}$  with aq. or alc.  $\text{NH}_4\text{OH}$  fails (1) to give chloroform;  $\bar{C}$  with  $\text{KOH}$  + aniline fails (1) to give phenylisocyanide. [Dif. from isomer 1,1,1-trichloropropanone-2 (3:5620).]

[ $\bar{C}$  with diazotized aniline in pres. of  $\text{NaOAc}$  couples (3) to yield a cpd. having composition  $\text{C}_6\text{H}_7\text{ON}_2\text{Cl}_3$  (and presumably structure  $\text{C}_6\text{H}_5\text{NH.N}=\text{C}(\text{Cl}).\text{CO}.\text{CHCl}_2$ ), cryst from pet. ether, m.p. 115-116° (3).]

3:5957 (1) Cloëz, *Ann. chim.* (6) 9, 176 (1886). (2) Akashi, *Bull. Inst. Phys.-Chem. Research (Tokyo)* 12, 329-340 (1933); *Cent.* 1933, I 3066; *C.A.* 27, 3147 (1933). (3) Favrel, *Bull. soc. chim.* (5) 1, 980-987, 989 (1934).

3:5960 *m*-DICHLOROBENZENE $\text{C}_6\text{H}_4\text{Cl}_2$ 

Bell. V - 202

V<sub>1</sub>-(111)V<sub>2</sub>-(154)

B.P.

F.P.

172.8° (1) -24° (0)  $D_4^{20} = 1.2879$  (11)  $n_D^{20} = 1.5470$  (11)

172.0-172.6° (2) -24.1° (12)

172-173° (7) -24.2° (12)  $D_4^{20} = 1.2881$  (8)

172° cor. at 760 mm. (3) -24.4° (8) 1.289 (11)

172.1° at 742.4 mm. (4) -21.8° (7) 1.287 (1)

169-176° at 755 mm. (5) -25° (5)  $n_D^{17.3} = 1.5472$  (8)170° cor. at 744 mm. (6) -26.25° (9)  $n_D^{17} = 1.5480$  (7)66° at 20 mm. (7) (10)  $D_4^{15} = 1.2937$  (8)

$\bar{C}$  when pure is colorless oil, volatile with steam.

[For f.p./compn. data and diagram of system  $\bar{C}$  + *o*-dichlorobenzene (3:6055) (eutectic, m.p. -45.9°, contg. 51.3%  $\bar{C}$ ) see (12); on system  $\bar{C}$  + *p*-dichlorobenzene (3:0980) (eutectic, m.p. -20.9°, contg. 88.0%  $\bar{C}$ ) see (12); for f.p./compn. data on ternary system of all three dichlorobenzenes see (7); for f.p./compn. data on systems:  $\bar{C}$  + fluorobenzene,  $\bar{C}$  + chlorobenzene (3:7903),  $\bar{C}$  + bromobenzene, and  $\bar{C}$  + *o*-chlorotoluene (3:8245) see (9).]

[For data on densities of solns. of  $\bar{C}$  in  $\text{C}_6\text{H}_6$  (1:7400) and in *n*-hexane (1:8530) see (13).]

[ $\bar{C}$  is very spar. sol. aq. (for study of this over range 20-60° see (14)).]

[For prepn. of  $\bar{C}$  from *m*-chloroaniline [Beil. XII-602, XII<sub>1</sub>-(300)] via diazotization and use of  $\text{Cu}_2\text{Cl}_2$  reactn. (yields: 80% (15), 70% (16)) (7) (17) or by pptn. of the diazonium chloroplatinate and hgt. of latter with  $\text{Na}_2\text{CO}_3$  (4) see indic. refs.; from 2,4-dichloroaniline [Beil. XII-621, XII<sub>1</sub>-(309)] via diazotization in alc. (18) (17) (3) (4) or isoamyl alc. (19) followed by replacement of orig. amino group by H by actn. of the alc. (60% yield (15)) or with hypophosphorous acid (50% yield (10)) (use of alk.  $\text{SnCl}_2$  or oxidn. of the corresp. 2,4-dichlorophenylhydrazine with  $\text{CuSO}_4$  gave only very low yields (15)) see indic. refs.; from *m*-phenylenediamine [Beil. XIII-33, XIII<sub>1</sub>-(10)] via totazotization in  $\text{AcOH}$  with

nitrosylsulfuric acid followed by use of  $\text{Cu}_2\text{Cl}_2$  reactn. (70.4% yield (20)) (21) see indic. refs.]

[For prepn. of  $\bar{\text{C}}$  from *m*-chloronitrobenzene [Beil. V-243, V<sub>1</sub>-(129)] with  $\text{SOCl}_2$  in s.t. at 190–200° for 12 hrs. (71% yield (22)), from *m*-nitrobenzenesulfonic acid [Beil. XI-68, XI<sub>1</sub>-(21)] with  $\text{SOCl}_2$  in s.t. at 180–200° (23), from *m*-bromonitrobenzene [Beil. V-248, V<sub>1</sub>-(131)] with  $\text{PCl}_5$  in s.t. at 180° (24), from 2,6-dichlorobenzoic acid (3:4200) by htg. in acetamide at 225–235° for 6 hrs. (93% yield (25)), or from 2,6-dichlorobenzaldehyde (3:1690) with 50% KOH under  $\text{N}_2$  at 100° for 5 hrs. (84% yield (6)) see indic. refs.]

[For formn. of  $\bar{\text{C}}$  from 2,6-dichloroacetophenone (5), 2,4-dichlorobenzophenone (3:0825) (26), 2,6-dichlorobenzophenone (3:2285) (26), or 3,5-dichlorobenzophenone (3:1505) (26) by fusion with KOH/NaOH see indic. refs.; for formn. of  $\bar{\text{C}}$  from 1,3-dichlorocyclohexadiene-1,3 [Beil. V-114] with  $\text{PCl}_5$  or with  $\text{Br}_2$  in  $\text{CHCl}_3$  see (27).]

[For formn. of  $\bar{\text{C}}$  from  $\text{C}_6\text{H}_6$  (1:7400) or chlorobenzene (3:7903) with  $\text{Cl}_2$  + cat. at 400–700° (50–60% yield (12)) (28) or with  $\text{Cl}_2$  in pres. of  $\text{AlCl}_3$  (29) cf. (30) see indic. refs.]

[ $\bar{\text{C}}$  with  $\text{Cl}_2$  +  $\text{Al}/\text{Hg}$  (31) or with  $\text{Cl}_2$  +  $\text{AlCl}_3$  (30) cf. (29) gives mainly 1,2,4-trichlorobenzene (3:6420). —  $\bar{\text{C}}$  suspended in 1% aq. NaOH adds 3  $\text{Cl}_2$  in sunlight giving (32) *m*-dichlorobenzene hexachloride, cryst. from alc., m.p. 81.8° (32). — For study of photochemical chlorination of  $\bar{\text{C}}$  see (33).]

[ $\bar{\text{C}}$  with Mg (1 mole) +  $\text{I}_2$  (0.25 equiv.) gave (34) after 3 days 62.5% *m*-chlorophenyl  $\text{MgCl}$ .]

[ $\bar{\text{C}}$  with  $\text{CHCl}_3$  +  $\text{AlCl}_3$  at 65° for 14 hrs. as directed gives (18% yield (35)) *tris*-(2,4-dichlorophenyl)methane, white cryst. from hot acetone, m.p. 227–228.5° (35). —  $\bar{\text{C}}$  with  $\text{CCl}_4$  +  $\text{AlCl}_3$  as directed gives (60% yield (35)) 2,4,2',4'-tetrachlorobenzophenone dichloride, white pl. from hot acetone, m.p. 139.0–140.5° (35), 140° (36); hydrolysis of this prod. with  $\text{AcOH}/\text{H}_2\text{SO}_4$  yields (37) 2,4,2',4'-tetrachlorobenzophenone, m.p. 78° (37), accompanied by some 2,4-dichlorobenzoic acid (3:4560), m.p. 161° (37).]

[ $\bar{\text{C}}$  with acetyl chloride (3:7065) +  $\text{AlCl}_3$  gives (15% yield (38)) 2,4-dichloroacetophenone, b.p. 140–150° at 15 mm. (33), m.p. 33–34° (33). —  $\bar{\text{C}}$  with chloroacetyl chloride (3:6235) +  $\text{AlCl}_3$  in  $\text{CS}_2$  yields (39) 2,4-dichlorophenacyl chloride (2,4- $\omega$ -trichloroacetophenone), pr. from lgr., m.p. 57° (39). —  $\bar{\text{C}}$  with  $\beta$ -chloro-*n*-butyric acid (3:0035) +  $\text{AlCl}_3$  or conc.  $\text{H}_2\text{SO}_4$  yields (40) by condens. and subsequent ring closure 4,6-dichloro-3-methylindanone-1, m.p. 67–70° (40). —  $\bar{\text{C}}$  with  $\alpha$ -bromobenzoyl chloride +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives (43% yield (41)) 2-bromo-2',4'-dichlorobenzophenone, b.p. 227–228.5°, m.p. 33–34°.]

[ $\bar{\text{C}}$  with phthalic anhydride +  $\text{AlCl}_3$  at 100–110° for 7 hrs. gives (17% yield on the anhydride (42)) (43)  $\alpha$ -(2,4-dichlorobenzoyl)benzoic acid, white cubes from  $\text{C}_6\text{H}_6$  or  $\text{CHCl}_3$ , m.p. 106–107° (42), 100–101° (43), accompanied (44) (especially if acetylene tetrachloride is used as solvent) by 3,3-bis-(2',4'-dichlorophenyl)phthalide, m.p. 176° (44); the above  $\alpha$ -(2,4-dichlorobenzoyl)benzoic acid with fuming  $\text{H}_2\text{SO}_4$  at 155–160° ring-closes (90% yield (42)) to 1,3-dichloroanthraquinone [Beil. VII-787, VII<sub>1</sub>-(411)], yel. ndls. from  $\text{AcOH}$ , m.p. 209–210° (42).]

[ $\bar{\text{C}}$  on hydrolysis with steam + cat. at 550–850° yields (45) *m*-chlorophenol (3:0255) and/or resorcinol (1:1530). — For studies of reactn. of  $\bar{\text{C}}$  with  $\text{NaOMe}/\text{MeOH}$  see (46) (47) (48).]

[ $\bar{\text{C}}$  with conc. aq.  $\text{NH}_4\text{OH}$  in pres. of  $\text{CuO}$  under press. at 150–200° (49) cf. (50) (51) yields *m*-phenylenediamine. —  $\bar{\text{C}}$  with  $\text{K}$  diphenylamine gives on htg. (16) (52)  $N,N,N',N'$ -tetraphenyl-*m*-phenylenediamine [Beil. XIH-42], m.p. 137.5–138° (16) (52) (note that this same prod. is similarly obtd. from  $\alpha$ -dichlorobenzene (3:0055) and in part also from *p*-dichlorobenzene (3:0980).]

[ $\bar{\text{C}}$  on mononitration, e.g., by soln. in 4.5 moles  $\text{HNO}_3$  ( $D = 1.5$ ) in cold followed by 10 min. htg. at 70° (53) or with 5 pts. fuming  $\text{HNO}_3$  ( $D = 1.52$ ) at 0° (90% yield (54)) cf.



(3) (27) (17) gives 1,3-dichloro-4-nitrobenzene [Beil. V-245,  $V_1$ -(131)], cryst. from alc., m.p. 34° (55), 33-34° (27), 33° (53) (3), accompanied by a little (2.6% at -30°, 4% at 0° (17)) 1,3-dichloro-2-nitrobenzene [Beil. V-246,  $V_1$ -(131)], m.p. 70.5° (55), 70° (56) (reactn. prod. with piperidine is 3-chloro-2-nitro-1-piperidinobenzene, m.p. 63° (57)).] — [The only other possible mononitro-*m*-dichlorobenzene, viz., 1,3-dichloro-5-nitrobenzene [Beil. V-246,  $V_1$ -(131)], m.p. 65° (55), has been prep'd. indirectly.]

$\bar{C}$  on dinitration, e.g., with 3.4 wt. pts.  $HNO_3$  ( $D = 1.54$ ) + 6.8 wt. pts. conc.  $H_2SO_4$  at 99° for 1 hr. (56) (cf. (22) (55) (27) (59) (60) (61)) gives (85% yield (56)) 1,3-dichloro-4,6-dinitrobenzene [Beil. V-265,  $V_1$ -(135)], cryst. from alc., m.p. 103° (22) (60), 102-103° (55), 102° (27), 101° (56), accompanied by 15% yield (56) of 1,3-dichloro-2,4-dinitrobenzene [Beil. V-265], m.p. 68° (56). — For f.p./compn. data and diagram for these two cpds. (eutectic, m.p. 48.1°, contg. 33% of the former) see (56). — Note that 1,3-dichloro-4,6-dinitrobenzene with piperidine in alc. boiled for 10 min. replaces 1 chlorine yielding (62) 1-chloro-4,6-dinitro-3-piperidinobenzene, yel. cryst. from alc., m.p. 119° (62); with piperidine in pyridine (requires cooling) it replaces both chlorine atoms yielding (62) 4,6-dinitro-1,3-dipiperidinobenzene, yel. lfts. from  $AcOH$ , m.p. 130-131° (62). — [Both of the other two possible dinitro-*m*-dichlorobenzenes are known, viz., 1,3-dichloro-2,5-dinitrobenzene [Beil.  $V_1$ -(135)], m.p. 114°, and 1,3-dichloro-4,5-dinitrobenzene [Beil. V-264], m.p. 98°, but have been prep'd. indirectly.]

[The direct trinitration of  $\bar{C}$  has not been reported; of the four possible trinitro-*m*-dichlorobenzenes only one, viz., 1,3-dichloro-2,4,6-trinitrobenzene [Beil. V-275], m.p. 128°, is known.]

$\bar{C}$  on monosulfonation with fuming  $H_2SO_4$  at 230° (3) or with fuming  $H_2SO_4$  (7%  $SO_3$ ) at 100° (7) or with fuming  $H_2SO_4$  (12%  $SO_3$ ) (54) gives (82% yield (54)) 1,3-dichlorobenzenesulfonic acid-4 [Beil. XI-55,  $XI_1$ -(15)], m.p. 86° (54) (corresp. sulfonyl chloride, m.p. 54.6° (7), corresp. sulfonamide, m.p. 182° (7) (see also below)), both  $\bar{C}$  and its *ortho* isomer (3:6055) sulfonate with about equal ease, both much more readily than *p*-dichlorobenzene (3:0980) (use in sepsns. from latter).]

$\bar{C}$  on disulfonation with fuming  $H_2SO_4$  (45%  $SO_3$ ) at 140-150° for 5 hrs. (63) gives 1,3-dichlorobenzenedisulfonic acid-4,0 (corresp. *bis*-(sulfonyl chloride), m.p. 122-123° (63) (64), corresp. *bis*-(sulfonamide), m.p. 276° (63); unlike the corresp. 1,3-dichloro-4,6-dinitrobenzene the halogen in this disulfonic acid is unreactive (63).]

[For study of kinetics of sulfonation of  $\bar{C}$  see (66).]

⑥ 1,3-Dichlorobenzenesulfonamide-4 (2,4-dichlorobenzenesulfonamide-1): cryst. from dil. alc., m.p. 179-180° u.c. (65). [From  $\bar{C}$  on treatment as directed (65) with  $Cl_2SO_2$  followed by conv. of the intermediate 1,3-dichlorobenzenesulfonyl chloride-4, m.p. 52-53° u.c. (65), to the sulfonamide by means of  $(NH_4)_2CO_3$ .] — [Note that although the m.p. of this sulfonamide is practically identical with that from *p*-dichlorobenzene (3:0980) each depresses the m.p. of a mixt. with the other; the m.p.'s of the precursor sulfonyl chlorides, viz., 52-53° for  $\bar{C}$ , 35° for the *p*-isomer, may also serve to distinguish them (65).]

3:5960 (1) Groves, Sugden, *J. Chem. Soc.* 1937, 1783. (2) Dadiou, Pongratz, Kohrausch, *Monatsh.* 61, 431 (1932). (3) Beilstein, Kurbatow, *Ann.* 182, 97-98 (1876). (4) Koerner, *Ber.* 66, 1530 (1937). (5) Lock, *Ber.* 66, 1530 (1937). (6) Lock, *Ber.* 66, 1530 (1937). (7) Lock, *Ber.* 66, 1530 (1937). (8) Narbutt, *Ber.* 66, 1530 (1937). (9) Narbutt, *Ber.* 66, 1530 (1937). (10) Timmermans, *Ber.* 66, 1530 (1937).

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359-360, 369-379 (1904). (18) Chattaway, Evans, *J. Chem. Soc.* 69, 850-851 (1896). (19) Raiford, Oberst, *Am. J. Pharm.* 107, 242-244 (1935). (20) Hodgson, Walker, *J. Chem. Soc.* 1935, 530.

(21) Sandmeyer, *Ber.* 17, 2652 (1884). (22) Davies, Hickox, *J. Chem. Soc.* 121, 2648-2649 (1922). (23) Kinziberger and Co., *Ger.* 280,379, Nov. 26, 1914; *Cent.* 1915, I 104. (24) Schmidt, Wagner, *Ann.* 387, 164-165 (1911). (25) Norris, Klemka, *J. Am. Chem. Soc.* 62, 1434 (1940). (26) Lock, Rodiger, *Ber.* 72, 868-870 (1939). (27) Crossley, Haas, *J. Chem. Soc.* 83, 502-503 (1903). (28) Wibaut, van der Lande, Wallagh (to Dow Chem. Co.), U.S. 2,123,857, July 12, 1938; *Cent.* 1939, I 250; *C.A.* 32, 7058 (1938). (29) Mouneyrat, Pourcet, *Compt. rend.* 127, 1027 (1898). (30) Olivier, *Rec. trav. chim.* 39, 411-413 (1920).

(31) Cohen, Hartley, *J. Chem. Soc.* 87, 1364 (1905). (32) von der Linden, *Ber.* 45, 415-416 (1922). (33) Fisk, Noyes, *J. Am. Chem. Soc.* 53, 1707-1714 (1936). (34) E. L. St. John, N. B. St. John, *Rec. trav. chim.* 55, 587 (1936). (35) Wilson, Cheng, *J. Org. Chem.* 5, 223-226 (1940). (36) Jaeger, *Z. anorg. allgem. Chem.* 101, 143-144 (1917). (37) Böseken, *Rec. trav. chim.* 27, 8-9 (1908). (38) Roberts, Turner, *J. Chem. Soc.* 1927, 1846. (39) Kunckell, *Ber.* 40, 1702-1703 (1907). (40) I.G., Swiss 126,404, June 16, 1928; 127,692-127,703, Sept. 1, 1928; 128,366, Oct. 16, 1928; *Cent.* 1929, I 1271-1272.

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19,844,  
1915),  
m. (3)  
Chem.  
Brit.

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— 1,3-DICHLOROPROPANONE-2  $\text{CH}_2\text{-C(=O)-CH}_2$   $\text{C}_3\text{H}_4\text{OCl}_2$  Beil. I - 655  
(sym.-Dichloroacetone)  $\begin{array}{c} \text{Cl} \quad \text{O} \quad \text{Cl} \\ | \quad || \quad | \end{array}$  I<sub>1</sub>-(344)  
I<sub>2</sub>-(719)

B.P. 173° M.P. 44°

See 3:0563. Division A: Solids.

3:5970  $\gamma$ -CHLORO-*n*-BUTYRYL CHLORIDE  $\text{C}_4\text{H}_7\text{OCl}_2$  Beil. II - 278  
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{C(=O)-}$  II<sub>1</sub>-(124)  
 $\begin{array}{c} \text{Cl} \quad \text{Cl} \\ | \quad | \end{array}$  II<sub>2</sub>-(254)

B.P. 173-174° (1)  $D_4^{20} = 1.2581$  (5)  $n_D^{20} = 1.4631$  (2)  
83-85° at 40 mm. (2) 1.46164 (5)  
68° at 15 mm. (3)  
60-61° at 12 mm. (4)  
55-56° at 12 mm. (5)  
59-60° at 11 mm. (6)

[For prepn. of  $\bar{C}$  from  $\gamma$ -chloro-*n*-butyric acid (3:0020) with  $\text{SOCl}_2$  (82% yield (4)) (3) in pet. etb. (6), or with  $\text{PCl}_5$  (1) (3), see indic. refs.: from *n*-butyryl chloride (3:7370) with  $\text{Cl}_2$  (7) or with  $\text{SO}_2\text{Cl}_2$  + dibenzoyl peroxide in  $\text{CCl}_4$  (30%  $\bar{C}$  + 15%  $\alpha$ - and 55%  $\beta$ -isomers (2)) see indic. refs.]

[ $\bar{C}$  with  $\text{EtZnI}$  at  $-15$  to  $-20^\circ$  yields (3)  $\gamma$ -chloro-*n*-propyl ethyl ketone (6-chlorohexanone-3) [Beil. I<sub>1</sub>-(355), I<sub>2</sub>-(747)], b.p.  $182$ – $183^\circ$  at  $761$  mm. (8) (semicarbazone, m.p.  $98$ – $99^\circ$  (8),  $118^\circ$  (3); *p*-nitrophenylhydrazone, m.p.  $106$ – $107^\circ$  (3)), but above  $0^\circ$  the reactn. yields  $\gamma$ -chloro-*n*-propyl-ethyl-carbinyl  $\gamma$ -chloroacetate, b.p.  $172$ – $174^\circ$  at  $19$  mm. (3).]

$\bar{C}$  on hydrolysis with aq. yields  $\gamma$ -chloro-*n*-butyric acid (3:0020).

For the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see  $\gamma$ -chloro-*n*-butyric acid (3:0020).

3:5970 (1) Henry, *Bull. soc. chim.* (2) 45, 341 (1886). (2) Kharasch, Brown, *J. Am. Chem. Soc.* 62, 925–929 (1940). (3) Wohlgemuth, *Ann. chim.* (9) 2, 307, 405–408 (1914). (4) Blicke, Wright, Zienty, *J. Am. Chem. Soc.* 63, 2489 (1941). (5) Leimu, *Ber.* 70, 1050 (1937). (6) Lipp, Caspers, *Ber.* 58, 1012–1013 (1925). (7) Michael, *Ber.* 34, 4051–4053 (1901). (8) Boesere, *Bull. soc. chim. Belg.* 32, 29 (1923).

3:5975 ISOPROPYL TRICHLOROACETATE  $\text{C}_5\text{H}_7\text{O}_2\text{Cl}_3$  Beil. S.N. 160  
( $\text{CH}_3$ )<sub>2</sub>CH.O.CO.CCl<sub>3</sub>

B.P.

173.9–174.9° (1)	$D_4^{25} = 1.2911$ (2)	$n_D^{25} = 1.4409$ (2)
173.5° at 747 mm. (2)	$D_4^{20} = 1.3034$ (3)	$n_D^{20} = 1.44355$ (3) cf. (5)
65.5–67.0° at 16 mm. (3)		
65° at 10 mm. (4)	$D_4^{15} = 1.2987$ (4)	$n_D^{15} = 1.4440$ (4)

[For prepn. from isopropyl alc. (1:6135) + trichloroacetic ac. (3:1150) (57.8% yield (2) (3)) see (2) (3); for prepn. from propylene + trichloroacetic ac. (3:1150) +  $\text{BF}_3$  (48.8% yield (2)) see (2).]

[For study of chlorination of  $\bar{C}$  see (4); for reaction with  $\text{C}_6\text{H}_6$  +  $\text{BF}_3$  yielding ethylbenzene (1:7410) see (6).]

[For study of hydrolysis of  $\bar{C}$  see (3).]

3:5975 (1) Cheng, *Z. physik. Chem. B-24*, 310 (1934). (2) Dorris, Sowa, Nieuwland, *J. Am. Chem. Soc.* 56, 2689–2690 (1934). (3) Palomaa, Salmi, Korte, *Ber.* 72, 797 (1939). (4) Gayler, Waddle, *J. Am. Chem. Soc.* 63, 3358–3359 (1942). (5) Schjanberg, *Z. physik. Chem. A-172*, 229 (1935). (6) McKenna, Sowa, *J. Am. Chem. Soc.* 59, 1204–1205 (1937).

— *p*-DICHLOROBENZENE



$\text{C}_6\text{H}_4\text{Cl}_2$

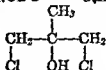
Beil. V - 203  
V<sub>1</sub>-(111)  
V<sub>2</sub>-(154)

B.P.  $174^\circ$  at  $764$  mm.

M.P.  $53^\circ$

See 3:0980. Division A: Solids.

3:5977 1,3-DICHLORO-2-METHYLPROPANOL-2  $C_4H_8OCl_2$  Boil. I-382  
(*sym.*-Dichloro-*ter*-butyl alcohol)



I<sub>1</sub>—  
I<sub>2</sub>—

B.P. 174-175°	(1)	$D_4^{20} = 1.2758$ (3)	$n_D^{20} = 1.4750$ (3)
173-174°	(2)	1.2745 (8)	1.47437 (8)
168-170.5° at 761 mm.	(3)		
72-73° at 23 mm.	(4)	$D_4^{19} = 1.266$ (6)	$n_D^{19} = 1.4662$ (6)
71-72° at 18 mm.	(5)		
73-75° at 15 mm.	(6)		
70° at 14.2 mm.	(7)		
69° at 14 mm.	(8)		
55-56° at 10 mm.	(3)		

[See also the isomeric 1,1-dichloro-2-methylpropanol-2 (3:5772).]

$\bar{C}$  with aq. forms a const.-boilg. mixt., b.p. 98.3°, contg. 35.2%  $\bar{C}$  (8). — Soly. of  $\bar{C}$  in aq. at 20° is 9.4 g.  $\bar{C}$  in 100 g. aq.; soly. of aq. in  $\bar{C}$  at 20° is 10.8 g. aq. in 100 g.  $\bar{C}$  (8).

### PREPARATION OF $\bar{C}$

[For prepn. of  $\bar{C}$  from 1-chloro-2-methylpropene-2 (methallyl chloride = isobutenyl chloride) (3:7145) by addn. of HOCl with HOCl (yields: 33% (4), 32% (3)) (7), with  $Cl_2$ /aq. (70% yield (8)), or with organic hypochlorites (7) see indie. refs.; note that if the initial methallyl chloride conts  $\beta,\beta$ -dimethylvinyl chloride (isocrotyl chloride) (3:7120) the crude HOCl addn. prod. will contain 1,1-dichloro-2-methylpropanol-2 (3:5772), but this can be separated from  $\bar{C}$  by fractional distillation]

[For prepn. of  $\bar{C}$  from  $\alpha,\alpha'$ -dichloroacetone (3:0563) with MeMgBr (yields: 80-85% (6), 40% (5)) (1) see indie. refs.; from chloroacetone (3:5425) with diazomethane via  $\beta$ -methyl epichlorohydrin (3-chloro-2-methyl-1,2-epoxypropane) (3:7657) and subsequent ring opening with conc. HCl see (2).]

### CHEMICAL BEHAVIOR OF $\bar{C}$

#### WITH INORGANIC REACTANTS

Dehydration. [ $\bar{C}$  is difficult to dehydrate but on twice htg. with equal wt.  $P_2O_5$  at 110-195° for 2 hrs. gives (46% yield (6)) 1,3-dichloro-2-methylpropene-1 (3:5590). —  $\bar{C}$  with strong  $H_2SO_4$  loses  $H_2O$  giving (9) 80% 3-chloro-2-(chloromethyl)propene-1 (3:5633) + 20% 1,3-dichloro-2-methylpropene-1 (3:5590).]

Dehydrohalogenation.  $\bar{C}$  with aq.  $Ca(OH)_2$  loses 1 HCl giving (93% yield (10) (11)) 3-chloro-2-methyl-1,2-epoxypropane ( $\beta$ -methylepichlorohydrin) (3:7657) which distils as its azeotrope, b.p. 89.8°, contg. 25.6% aq. (10). — Note that, if alk. is added in excess, reactn. is complete in a few seconds at room temp. and the process can even be used as a method for detn. of  $\bar{C}$  in aq. soln. [For use of  $\bar{C}$  in comml. prepn. of  $\beta$ -methylepichlorohydrin (3:7657),  $\beta$ -methylglycerol monochlorohydrin,  $\beta$ -methylglycidol, and  $\beta$ -methylglycerol see (10).]

Behavior with sodium sulfite. [ $\bar{C}$  (1 mole) with aq.  $Na_2SO_3$  (2 moles) at 70-90° for 2 hrs. yields (3) the salt of 2-methylpropanol-2-disulfonic acid-1,3; this prod. with  $PCl_4$  not only is converted to the bis (acid chloride) but simultaneously loses  $H_2O$  yielding (3) 2-methylpropen-1,3-bis-(sulfonyl chloride), long n.dls. from  $CCl_4$ ,  $C_6H_6$ , or pet. ether, m.p.

[For prepn. of  $\bar{C}$  from o-dichlorobenzene (3:6055) by partial hydrol. with aq. MeOH or EtOH alk., alk. earths, or alk. carbonates in pres. of Cu or Cu salts at elevated temps. under press. see (38)-(46) incl.]

[ $\bar{C}$  in excess dil. aq. KOH with  $H_2$  in pres. of Ni absorbs 1 mole  $H_2$  (47) but more slowly than m-chlorophenol (3:0255) or p-chlorophenol (3:0475). —  $\bar{C}$  is not reduced with HI in AcOH at 25° (48).]

[ $\bar{C}$  on oxidn. with 35% persacetic acid at 25° gives slowly (17 days) in small yield (49) o-chloromuconic acid (2-chlorobutadiene-1,3-dicarboxylic acid-1,4), m.p. 190° (49), ÷ 5-chlorohexadiene-2,4-al-6-oic acid-1, m.p. 145° (49).]

[ $\bar{C}$  with  $Cl_2$  (2 moles) in AcOH gives (80% yield (50)) 2,4-dichlorophenol (3:0560);  $\bar{C}$  with  $Cl_2$  (3 moles) undoubtedly gives 2,4,6-trichlorophenol (3:1673). — For study of chlorination of  $\bar{C}$  with HOCl see (51).]

$\bar{C}$  with  $Br_2$  (1 mole) in  $CCl_4$  gives (87% yield (52)) 4-bromo-2-chlorophenol, ndls. from lgr., m.p. 48–49° (52), 49–50° (53), 50–51° (54). —  $\bar{C}$  with  $Br_2$  (2 moles) in aq. KBr soln. gives (55) 2-chloro-4,6-dibromophenol [Beil. VI-203], ndls. from alc., m.p. 76° cor. (53), 75–76° (56). —  $\bar{C}$  with large excess  $Br_2$  in pres. of Fe powder gives (57) 2-chloro-3,4,5,6-tetrabromophenol, ndls. from alc. or AcOH, m.p. 224° (57).

[ $\bar{C}$  in aq. alk. with  $I_2/KI$  soln. as directed (55) gives 2-chloro-4,6-di-iodophenol, ndls. from alc., m.p. 96° (55). — For study of iodination of  $\bar{C}$  see (58).]

[ $\bar{C}$  on nitrosation as directed (59) (60) gives (96% yield (60)) 2-chloro-4-nitrosophenol (2-chlorobenzoquinone-1,4-oxime-4) [Beil. VII-631, VII<sub>r</sub>-(346)], pale yel. ndls. from  $C_6H_6$ , m.p. 145° (60), 142° (59); for discussion of tautomerism of this cpd. see also (61) (62) (63).]

[ $\bar{C}$  on mononitration, e.g., with cold mixt. of equal pts.  $HNO_3$  ( $D = 1.36$ ) ÷ aq. (13), with  $HNO_3$  in MeOH (64), or with  $HNO_3$  ( $D = 1.5$ ) in AcOH (65), gives a mixt. of 2-chloro-4-nitrophenol [Beil. VI-240], ndls. from aq., m.p. 110–111°, and (32% (65)) 2-chloro-6-nitrophenol [Beil. VI-239], ndls. from aq., m.p. 70–71°; of these only the latter is volatile with steam (use in detn. of  $\bar{C}$  in mixts. with 4-chlorophenol (3:0475) (27)). — Both of the other mononitro-o-chlorophenols are known but have been obtd. only by indirect means; e.g., 2-chloro-3-nitrophenol, m.p. 120.5° (66), 120° (67), and 2-chloro-5-nitrophenol, m.p. 119.5° (66).]

$\bar{C}$  on dinitration, e.g., by soln. in  $HNO_3$  ( $D = 1.36$ ) and subsequent warming yields (68) 2-chloro-4,6-dinitrophenol [Beil. VI-259, VI<sub>r</sub>-(125)], cryst. from alc., m.p. 113° (68); this prod. (unlike picric acid) is volatile with steam from  $H_2SO_4$  soln. (use in anal. of mixts. of  $\bar{C}$  with phenol (17)).

[ $\bar{C}$  in alk. soln. couples with diazotized aniline giving (70% yield (69) (70) (71)) 3-chloro-4-hydroxyazobenzene (2-chlorobenzoquinone phenylhydrazone-4) [Beil. XVI-120], yel. pr. from aq. alc., m.p. 88.5° (69), 88° (70), 86° (71). — For study of corresp. coupling of  $\bar{C}$  with diazotized p-nitrosaniline see (72).]

[For mercuration of  $\bar{C}$  and use of products as seed disinfectants, etc., see (73); for condens. prods. of  $\bar{C}$  with  $C_6H_5Hg.OH$  see (74).]

[ $\bar{C}$  over pumice in a silica tube at dull red heat (75) or K salt of  $\bar{C}$  + K phenolate at 250° for 8 hrs. (81) yields diphenylene dioxide [Beil. XIX-44, XIX<sub>r</sub>-(618)], ndls. from MeOH, m.p. 119°, readily identified by dinitration with fuming  $HNO_3$  in AcOH (75) to dinitrodiphenylene dioxide, ndls. from pyridine, m.p. 257° (75).]

Condensation reactions involving nuclear hydrogens. [ $\bar{C}$  with formalin (1:0145) in pres. of conc. HCl treated with HCl gas as directed (76) gives 3-chloro-4-hydroxybenzyl chloride, m.p. 92–93° (76). —  $\bar{C}$  with formalin +  $H_2SO_4$  (60%) at 60–65° for 16 hrs. gives (76) 3,3'-dichloro-4,4'-dihydroxydiphenylmethane, m.p. 103–104° (76). —  $\bar{C}$  with formalin (1:0145) + aq. 10% NaOH as directed (77) yields acc. to conditions 3-chloro-4-hydroxybenzyl alc., pl. from  $C_6H_6$ , m.p. 123.5–124°, and/or 3-chloro-4-hydroxy-5-(hydroxymethyl)-

benzyl alc., ndls. from  $\text{CHCl}_3$ , m.p. 117.5–119°. — For condens. of  $\tilde{\text{C}}$  with formalin in prepn. of synthetic tanning agents see (78).]

[ $\tilde{\text{C}}$  with  $\text{CHCl}_3$  or  $\text{CHBr}_3$  (79) in pres. of aq.  $\text{NaOH}$  undergoes Reimer-Tiemann reaction yielding both 3-chloro-2-hydroxybenzaldehyde (3:1010) and 3-chloro-4-hydroxybenzaldehyde (3:4065). —  $\tilde{\text{C}}$  with  $\text{CCl}_4$  in alc. alk. in s.t. at 125–136° yields (80) 3-chloro-4-hydroxybenzoic acid (3:4675). —  $\tilde{\text{C}}$  with  $\alpha, \alpha$ -dichlorodiphenylmethane (3:6960) +  $\text{AlCl}_3$  in cold  $\text{CS}_2$  gives (31) 3-chloro-4-hydroxyphenyl-diphenyl-carbinol, from 60%  $\text{AcOH}$  as deep orange pl. of quinonoid desmotrope, m.p. 118°, but from alc. colorless crystals of benzenoid desmotrope (contg.  $\frac{1}{2}$  mole solvent), m.p. 70–72° (31); note that in hot  $\text{C}_6\text{H}_6$ , however, this reaction takes a different course yielding (31)  $\alpha, \alpha$ -bis-(*o*-chlorophenoxy)diphenylmethane, cryst. from hot alc., m.p. 191–192° (31). —  $\tilde{\text{C}}$  with chloral hydrate (3:1270) in pres. of alk. salts condenses (82) to 3-chloro-4-hydroxyphenyl-trichloromethyl-carbinol which on hydrolysis with  $\text{NaOH}$  yields 3-chloro-4-hydroxybenzaldehyde (3:4065).]

[ $\tilde{\text{C}}$  with  $\text{SOCl}_2$  +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives (85% yield (83)) *bus*-(3-chloro-4-hydroxyphenyl) sulfoxide [Beil. VI-422], ndls. from dil. alc. contg.  $\text{HCl}$ , m.p. 195°. —  $\tilde{\text{C}}$  with mixt. of conc.  $\text{H}_2\text{SO}_4$  + fuming  $\text{H}_2\text{SO}_4$  (25%  $\text{SO}_3$ ) at 100° for 6 hrs. disulfonates to 2-chloro-4,6-disulphophenol which undergoes bimolecular condensation to the corresp. internal ester (for details see (84)).]

[ $\tilde{\text{C}}$  with phthalic anhydride (1:0725) with  $\text{AlCl}_3$  in acetylene tetrachloride (3:5750) (85) (86) (87), or with  $\text{AlCl}_3$  +  $\text{NaCl}$  at 150° (88), gives (yields: 96% (85) (86), 87% (88)) 2-(3'-chloro-4'-hydroxybenzoyl)benzoic acid, cryst. from  $\text{MeOH}$ , m.p. 224–225° (85), cryst. from  $\text{AcOH}$ , m.p. 219.5–220° (86), 219° (88); this prod. on ring closure with 15 pts. conc.  $\text{H}_2\text{SO}_4$  at 150° for 1 hr. (88), or with 10 pts. conc.  $\text{H}_2\text{SO}_4$  + 1 pt.  $\text{ZnCl}_2$  at 130° for  $5\frac{1}{2}$  hrs. (85), or with 16 pts. 100%  $\text{H}_2\text{SO}_4$  + 1 pt.  $\text{H}_3\text{BO}_3$  at 195° for  $1\frac{1}{2}$  hrs. (86), gives (yields. 80% (85), 76% (88), 53.5% (86)) 3-chloro-2-hydroxyanthraquinone, yel. ndls. from  $\text{AcOH}$ , nitrobenzene +  $\text{AcOH}$ , or xylene, m.p. 267–268° (85), 266.5–267° (86), 266° (88). — Note that by slight variations other products are also formed; e.g.,  $\tilde{\text{C}}$  + phthalic anhydride + fuming  $\text{H}_2\text{SO}_4$  +  $\text{H}_3\text{BO}_3$  at 170–200° for 10 hrs. gives (89) both chloro-hydroxy-anthraquinone and dihydroxyanthraquinone cf. (90) and at 255° gives (91) 1,2,4-trihydroxyanthraquinone (purpurin). — Note that  $\tilde{\text{C}}$  (2 moles) with phthalic anhydride (1 mole) at 125° for 6 hrs. gives (75% yield (92)) dichlorophenolphthalein, m.p. 98°.]

Reactions of nuclear halogen of  $\tilde{\text{C}}$ . [ $\tilde{\text{C}}$  on hydrolysis with aq. alk., alk. carbonates, or alkaline earths in pres. of cat. such as  $\text{Cu}$  or  $\text{Cu}$  salts at elevated temps. and under press. yields (93) (94) (95) (96) (97) (98) pyrocatechol (1:1520) cf. (43). —  $\tilde{\text{C}}$  on fusion with  $\text{KOH}$  yields (13) pyrocatechol but some resorcinol (1:1530) is also formed (88) (99). —  $\tilde{\text{C}}$  with aq.  $\text{Na}_2\text{S}$  +  $\text{NaOH}$  at 210–215° for 24 hrs. yields (100) 2-mercaptophenol [Beil. VI-793], b.p. 216–217° corr., m.p. +5°.]

Reactions of the phenolic group of  $\tilde{\text{C}}$  (see also under @, below).  $\tilde{\text{C}}$  behaves as a weak acid; e.g.,  $\tilde{\text{C}}$  dis. in conc. aq.  $\text{Na}_2\text{CO}_3$  soln. on shaking at room temp. (dif. and sepn. from phenol (18)) and is reprecip. by treatment with  $\text{CO}_2$  (18). — Dissoc. const. of  $\tilde{\text{C}}$  in aq. =  $32 \times 10^{-10}$  (101); for studies of dissoc. const. in 50%  $\text{MeOH}$  at 20° (7) (101) (102), in 25%  $\text{EtOH}$  at 25° (103), in 30%  $\text{EtOH}$  at 25° (4) (102) see indic. refs.

$\tilde{\text{C}}$  has bactericidal (104) (105) (106) (107) (108) (109) and fungicidal (110) properties.

[ $\tilde{\text{C}}$  with alkali metals gives corresp. alk. *o*-chlorophenolates; for use of these as antioxidants in motor fuels see (111). — Dry  $\text{Na}$  *o*-chlorophenolate with  $\text{CO}_2$  at 140–150° under press. yields (25) 3-chloro-2-hydroxybenzoic acid (3-chlorosalicylic acid) (3:4745).]

[ $\tilde{\text{C}}$  in  $\text{MeOH}/\text{KOH}$  with  $\text{MeI}$  in s.t. at 130° (112), or  $\tilde{\text{C}}$  with aq.  $\text{KOH}$  +  $\text{Me}_2\text{SO}_4$  at ord. temp. (113), yields *o*-chlorophenyl methyl ether (*o*-chloroanisole) (3:6255). —  $\tilde{\text{C}}$  in abs. alc. +  $\text{NaOEt}$  with  $\text{EtI}$  yields (115) *o*-chlorophenyl ethyl ether (*o*-chlorophenetole) (3:8735). —  $\tilde{\text{C}}$  with alkyl bromide in acetone + aq. +  $\text{NaOH}$  gives (90% yield (146))

allyl *o*-chlorophenyl ether; b.p. 103–110° at 15 mm.,  $D_{25}^{25} = 1.132$ ,  $n_D^{25} = 1.5388$ ; this prod. on reflux. 10 min. gives by Claisen rearr. (89% yield (146)) 2-chloro-6-allylphenol, b.p. 61–63° at 1 mm.,  $n_D^{25} = 1.5447$ .]

[ $\bar{C}$  with  $POCl_3$  refluxed for 8–11 hrs.,  $POCl_3$  distd. off, and crude product saponified yields (117) *bis*-(*o*-chlorophenyl)phosphoric acid, m.p. 105–106° cor. — For condens. of  $\bar{C}$  with triphenylphosphine oxide and use of prod. as seed disinfectant see (118); for use of  $\bar{C}$  in prepn. of triaryl phosphates (119) or of mixed triaryl thiophosphates (120) and use as plasticizers see indic. refs. —  $\bar{C}$  with  $PCl_5$  gives on htg. (22) *o*-dichlorobenzene (3:6055).]

[ $\bar{C}$  with malic acid (1:0450) + conc.  $H_2SO_4$  fails (121) to give the expected von Pechmann synthesis of 8-chlorocoumarin; however,  $\bar{C}$  with  $\alpha$ -substituted acetoacetic esters +  $P_2O_5$  condenses to corresp. chromones; e.g.,  $\bar{C}$  with ethyl  $\alpha$ -methylacetoacetate (1:1712) +  $P_2O_5$  gives (27% yield (122)) 8-chloro-2,3-dimethylchromone [Beil. XVII<sub>1</sub>-(177)], pale yel. ndls. from dil. alc., m.p. 103°; for further examples see (123). —  $\bar{C}$  (as sodium salt) + diethyl fumarate (1:3761) refluxed in xylene yields (124) diethyl  $\alpha$ -(*o*-chlorophenoxy)-fumarate which on subsequent hydrolysis to the acid, ring closure with conc.  $H_2SO_4$ , and decarboxylation gives 8-chlorochromone, colorless ndls., m.p. 114–115° (124).]

$\bar{C}$  with  $AlCl_3$  evolves  $HCl$  and yields (125)  $Cl.C_6H_4.O.AlCl_2$ , insol.  $CS_2$ , but sol. in alc. and hydrolyzed by aq., m.p. 207–210° (125). —  $\bar{C}$  in 50% alc. with satd. soln. of  $KOH$  in 50% alc. yields (126) a mol. cpd.,  $\bar{C}.KOH$ , pale yel. ndls., m.p. 81–82° (126).

⑥  $FeCl_3$  color reaction:  $\bar{C}$  in aq. soln. with very dil.  $FeCl_3$  gives violet coloration;  $\bar{C}$  in alc. with very dilute aq.  $FeCl_3$  gives greenish-blue.

— *o*-Chlorophenyl acetate: oil, b.p. 103° cor. at 15 mm.,  $D_4^{20} = 1.2166$  (18). [From  $\bar{C}$  with  $Ac_2O$  (4 pts.) +  $NaOAc$  (1 pt.) boiled for 10 min. (18).]

— *o*-Chlorophenyl benzoate [Beil. IX-117]: oil, b.p. 314–316° (?) (127), 212–213° at 745 mm. (127), 155–157° at 3 mm. (127). [From  $\bar{C}$  + benzoyl chloride + aq.  $NaOH$  (127) (for study of rate see (129)).] [Note also that  $\bar{C}$  +  $BzCl$  +  $AlCl_3$  in acetylene tetrachloride yields (128) the Fries rearr. prods. to be expected from *o*-chlorophenyl benzoate, viz., 3-chloro-4-hydroxybenzophenone, cryst. from alc. or  $C_6H_6$ , m.p. 180–181° (128), and 3-chloro-2-hydroxybenzophenone, pale yel. cryst. from alc., m.p. 92.5–93° (128).]

⑦ *o*-Chlorophenyl *m*-nitrobenzoate: pr. from 1gr., m.p. 98° (18). [From  $\bar{C}$  with *m*-nitrobenzoyl chloride on shaking with 10% aq.  $NaOH$  at 35–50° (18).]

— *o*-Chlorophenyl *p*-nitrobenzoate: ndls. from 85% alc., m.p. 114.5–114.8°. [From  $\bar{C}$  + *p*-nitrobenzoyl chloride in pyridine (unpublished work).]

— *o*-Chlorophenyl 3,5-dinitrobenzoate: ndls. from 85% alc., m.p. 143.1–143.4°. [From  $\bar{C}$  + 3,5-dinitrobenzoyl chloride in pyridine (unpublished work).]

— *o*-Chlorophenyl benzenesulfonate: unrecorded.

— *n*-Chlorophenyl *p*-toluenesulfonate: m.p. 74° (4).

— *o*-Chlorophenyl benzyl ether: oil, b.p. 133–140° at 3 mm. (130). [From  $\bar{C}$  (as Na salt) + benzyl chloride but in very poor yield (7.5% (130)); note that the products elsewhere (131) (132) seem to be questionable.]

— *o*-Chlorophenyl *p*-nitrobenzyl ether: m.p. 100° (133). [From  $\bar{C}$  (as Na salt) with *p*-nitrobenzyl bromide refluxed in aq. alc. (133).]

⑧ *o*-Chlorophenyl 2,4-dinitrophenyl ether: greenish-yel. ndls. from alc., m.p. 99° (134). [From  $\bar{C}$  in equiv. amt. aq.  $NaOH$  refluxed with alc. 2,4-dinitrochlorobenzene (134). — Note that the m.p. of 75–76° reported earlier (135) for this compd. is identical with that given later (134) for the corresp. deriv. of *m*-chlorophenol (3:0255).]

⑨ *o*-Chlorophenoxyacetic acid (3:4375): m.p. 145–146° (136) (137), 143–145° (138); Neut. Eq. 186.5. [From  $\bar{C}$  in aq.  $NaOH$  (2 equivs.) with chloroacetic acid (1 equiv.) refluxed for 1 hr., then acidified (138) cf. (136) (137).]

- ③ *o*-Chlorophenyl *N*-(phenyl)carbamate: cryst. from  $C_6H_6$ , m.p. 120–121° (139). [From  $\bar{C}$  + phenyl isocyanate in dry ether (139).]
- ④ *o*-Chlorophenyl *N*-(*p*-iodophenyl)carbamate: m.p. 156–157° (147). [From  $\bar{C}$  + *p*-iodobenzazide in hot lgr. (147).]
- ⑤ *o*-Chlorophenyl *N*-(*p*-bromophenyl)carbamate: pr. from EtOAc, m.p. 141–143° cor. (140). [From  $\bar{C}$  + *p*-bromobenzazide in lgr. (140).]
- ⑥ *o*-Chlorophenyl *N*-(*m*-nitrophenyl)carbamate: m.p. 114° u.c., 116° cor. (148). [From  $\bar{C}$  + *m*-nitrobenzazide (148) or *m*-nitrophenyl isocyanate (148) in lgr. (148).]
- ⑦ *o*-Chlorophenyl *N*-(*p*-nitrophenyl)carbamate: ndls. from lgr., m.p. 143° cor. (141). [From  $\bar{C}$  + *p*-nitrobenzazide in lgr. (141).] — [Note that corresp. deriv. of *m*-chlorophenol (3:0255) has m.p. 144° cor. (141).]
- ⑧ *o*-Chlorophenyl *N*-(3,5-dinitrophenyl)carbamate: pl. from  $C_6H_6$ , m.p. 182–183° (142). [From  $\bar{C}$  + 3,5-dinitrobenzazide htd. in dry toluene (142).]
- ⑨ *o*-Chlorophenyl *N*-(3,5-dinitro-4-methylphenyl)carbamate: yel. pl. from lgr. or EtOAc, m.p. 175–176°, u.c., 180–181° cor. (143). [From  $\bar{C}$  + 3,5-dinitro-4-methylbenzazide in lgr. (143).]
- ⑩ *o*-Chlorophenyl *N*-( $\alpha$ -naphthyl)carbamate: cryst. from lgr., m.p. 120° (144). [From  $\bar{C}$  +  $\alpha$ -naphthyl isocyanate in lgr. (144).]
- ⑪ *o*-Chlorophenyl *N*-( $\beta$ -naphthyl)carbamate: pl. from lgr., m.p. 133–134° u.c., 136–137° cor. (145). [From  $\bar{C}$  +  $\beta$ -naphthyl isocyanate (or azide) in lgr. (145).]
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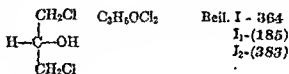
(126) *Moyle*, *Helv.* 11, 1144 (1919). (127) *Moyle*, *Helv.* 11, 1144 (1919). (128) *Moyle*, *Helv.* 11, 1144 (1919). (129) *Moyle*, *Helv.* 11, 1144 (1919). (130) *Moyle*, *Helv.* 11, 1144 (1919).

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3:5985 1,3-DICHLOROPROPANOL-2  
 ( $\beta,\beta'$ -Dichloroisopropyl alcohol;  
 glycerol  $\alpha,\alpha'$ -dichlorohydrin;  
 "alpha-dichlorohydrin")



B.P.

175.8-176.3° at 765 mm. (1)	$D_4^{25} = 1.359$ (2) (6)	$n_D^{25} = 1.4797$ (2)
176° at 760 mm. (2) (6)		
175.1° at 760 mm. (3)		$n_D^{20} = 1.4837$ (45)
175.5-176° at 733 mm. (4)		
174.3° at 760 mm. (5)	$D_4^{17} = 1.3506$ (9)	$n_D^{15} = 1.48025$ (9)
92-92.5° at 40 mm. (2) (6)		
86° at 32 mm. (7)		
75° at 12 mm. (8)		
70-73° at 14 mm. (10)		
69° at 12 mm. (45)		

Note: Because of the great magnitude of the literature of  $\bar{C}$  only the most important citations can be included here; for much additional data prior to 1930, the appropriate volume of Beilstein should also be consulted.

$\bar{C}$  dis. at 19° in 9 pts. aq.; at 72° in 6 pts. aq., misc. with ether. [For recovery of  $\bar{C}$  from aq. solns. by extraction with immiscible solvents (12) (13) (14) or by steam distillation (12) (15) see indic. refs.]

[For prepn. of  $\bar{C}$  from glycerol (1:6540) by actn. of HCl gas at 100-110° (yield: 87% (11), 82% (6), 55-57% (10)) (12) see indic. refs.; for prepn. of  $\bar{C}$  from 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358) with fuming HCl (yield 80% (11)) (16) (17) (1) (18), with  $\text{MgCl}_2$  in dil. alc. at 125° (19), or with  $\text{S}_2\text{Cl}_2$  (67% yield (40)) see indic. refs.; for formn. of  $\bar{C}$  (together with other prods.) from glycerol (1:6540) with  $\text{SOCl}_2$  + pyridine see (20); from corresp. acetate (3:6318) by alcoholysis with MeOH + HCl see (21) (45); from  $\alpha,\alpha'$ -dichloroacetone (3:0563) reductn. with yeast see (22).]

$\bar{C}$  with aq. alk. rapidly loses HCl giving 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358) (yield: 90% (6), 80-90% (23), 76-81% (24-B), 67-72% (24-A), 85% (25), 79% (26)).

$\bar{C}$  on oxidn. with  $\text{Na}_2\text{Cr}_2\text{O}_7$  +  $\text{H}_2\text{SO}_4$  gives (68-75% yield (27))  $\alpha,\alpha'$ -dichloroacetone (3:0563). (Overoxidn. of this prod. or  $\bar{C}$  on oxidn. with conc.  $\text{HNO}_3$  (28) gives chloroacetic acid (3:1370).]

[ $\bar{C}$  on reductn. with Na/Hg in moist ether gives various products including allyl alc. (1:0145), isopropyl alc. (1:6135), propylene together with epichlorohydrin (for refs. see Beil. I-364);  $\bar{C}$  htd. with III + P in s.t. at 180° gives (29) isopropyl iodide.]

[For behavior of  $\bar{C}$  with NaSH yielding 1,3-dithioglycerol (Hg deriv. m.p. 185°, Pb deriv. m.p. 175–180° dec.) see (41).]

$\bar{C}$  on hgt. with  $P_2O_5$  (31) or  $POCl_3$  (11) (30) yields 1,3-dichloropropene-1 (3:5280).

$\bar{C}$  on hgt. with excess EtOH + NaOH yields (by a series of definite intermediate stages (25)) (0) 1,3-diethoxypropanol-2 (glycerol  $\alpha,\gamma$ -diethyl ether) b.p. 108–111° at 60 mm.,  $D_4^{25} = 0.953$ ,  $n_D^{25} = 1.420$  (10) (0); similarly  $\bar{C}$  on hgt. with excess phenol + aq. NaOH as specified (19) gives 80% yield 1,3-diphenoxypropanol-2 (glycerol  $\alpha,\gamma$ -diphenyl ether), cryst. from alc., m.p. 80–81° (10).

—  $\beta,\beta'$ -Dichloroisopropyl acetate: b.p. 205° (see 3:6318).

—  $\beta,\beta'$ -Dichloroisopropyl benzoate: b.p. 296° sl. dec. (12); 171–173° at 10 mm. (43), 157–160° at 12 mm. (44). [From  $\bar{C}$  + benzoyl chloride on hgt. (42) or with pyridine (44).]

①  $\beta,\beta'$ -Dichloroisopropyl *p*-nitrobenzoate: m.p. 50–60° (32), 58–59° (33). [From  $\bar{C}$  + *p*-nitrobenzoyl chloride with pyridine (94% yield) (33) or with quinoline in  $CHCl_3$  (100% yield) (32).]

②  $\beta,\beta'$ -Dichloroisopropyl 3,5-dinitrobenzoate: m.p. 129° (32). [From  $\bar{C}$  + 3,5-dinitrobenzoyl chloride + quinoline in  $CHCl_3$  in 100% yield (32).]

③  $\beta,\beta'$ -Dichloroisopropyl benzenesulfonate: long colorless ndls. from  $C_6H_6$ , m.p. 50° (34). [From  $\bar{C}$  + benzenesulfonyl chloride + conc. aq. NaOH (34); for study of pyrolysis see (35).]

④  $\beta,\beta'$ -Dichloroisopropyl *p*-toluenesulfonate: m.p. 52–53° (36). [From  $\bar{C}$  + *p*-toluenesulfonyl chloride with conc. aq. NaOH (36).] [For use in prepn. of vat dyes of dibenzanthrone series see (37).]

⑤  $\beta,\beta'$ -Dichloroisopropyl *N*-(phenyl)carbamate: m.p. 73–74° (20) (38), 73° (39). [From  $\bar{C}$  with phenyl isocyanate (20) (39); also indirectly from  $\bar{C}$  by conv. to corresp. chloroformate and reacting with aq. anilino (38).] [This prod. htd. a few min. with conc. aq. KOH loses HCl and ring-closes alm. quant. to 5-chloromethyl-3-phenyloxazolidone-2, pr. from hot alc., m.p. 101–105° (39).]

⑥  $\beta,\beta'$ -Dichloroisopropyl *N*-( $\alpha$ -naphthyl)carbamate: m.p. 115° (38). [Prepd. indirectly from  $\bar{C}$  by conv. to corresp. chloroformate and reacting with aq. anilino (38).] [This prod. with conc. aq. alk. loses HCl and ring-closes to 5-chloromethyl-3-( $\alpha$ -naphthyl)-oxazolidone-2, m.p. 118° (38).]

⑦  $\beta,\beta'$ -Dichloroisopropyl *N*-( $\beta$ -naphthyl)carbamate: m.p. 101° (38). [Prepd. indirectly from  $\bar{C}$  by conv. to corresp. chloroformate and reacting with aq. anilino (38).] [This prod. with conc. aq. alk. loses HCl and ring-closes to 5-chloromethyl-3-( $\beta$ -naphthyl)-oxazolidone-2, m.p. 107° (38).]

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## CHAPTER XIV

### DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

#### Section 1. $D_4^{20}$ greater than 1.1500

(3:6000-3:6499)

3:6000	<i>n</i> -PROPYL DICHLOROACETATE	$C_5H_9O_2Cl_2$	Beil. II - 204
	<i>n</i> -C <sub>3</sub> H <sub>7</sub> O.CO.CHCl <sub>2</sub>		II <sub>1</sub> — II <sub>2</sub> -(196)
B.P. 176.7-177°	at 771 mm. (1)	$D_4^{25} = 1.2006$ (4)	$n_D^{25} = 1.4369$ (4)
176.0-176.6°	(2)	$D_4^{20} = 1.2240$ (5)	$n_D^{20} = 1.4398$ (5)
176°	(3)		

[For prepn. (70% yield (3)) from anhydrous chloral (3:5210) in *n*-propyl alc. by treatment with 1.2 moles powdered KCN see (3); for prepn. (59% yield (4)) from cyclopropane + dichloroacetic ac. (3:6208) + BF<sub>3</sub> see (4).]

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2, 229 (1935)

3:6010	$\gamma$ -CHLORO- <i>n</i> -PROPYL CHLOROFORMATE	$C_4H_7O_2Cl_2$	Beil. S.N. 199
	( $\gamma$ -Chloro- <i>n</i> -propyl chlorocarbonate)	$CH_2CH_2CH_2O.CO.Cl$	
		$\begin{array}{c}   \\ Cl \end{array}$	
B.P. 177°	(1)	$D_{20}^{25} = 1.2946$ (1)	$n_D^{20} = 1.4456$ (1)
175-176°	at 736 mm. (2)		

Colorless liq.; insol. in aq. toward which it is relatively stable.

[For prepn. of  $\bar{C}$  from 3-chloropropanol-1 (trimethylene chlorohydrin) (3:8285) with phosgene (3:5000) in 80% yield see (1) (2).]

$\bar{C}$  in quinoline begins to decompose into 1,3-dichloropropane (trimethylene (di)chloride) (3:5450) + CO<sub>2</sub> even at 35° (3) (for discussion see (4)).

$\bar{C}$  with primary arom. amines reacts as an acyl chloride yielding the corresp.  $\gamma$ -chloro-*n*-propyl *N*-arylcarbamates [e.g.,  $\bar{C}$  with *p*-aminobenzenearsonic acid (arsanilic acid) gives (92% yield (5))  $\gamma$ -chloro-*n*-propyl *N*-(*p*-arsonophenyl)carbamate, m.p. 245-246° (5) cf. (6); for analogous reactions of  $\bar{C}$  with *o*-aminobenzenearsonic acid (5) (6), *o*-toluidine-5-arsonic acid (5), *p*-phenetidine (1), *p*-aminobenzoic acid (1), *o*-chloroaniline (1), or *p*-chloroaniline (1) see indic. refs.]; for simpler cases see below.

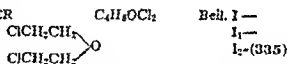
①  $\gamma$ -Chloro-*n*-propyl carbamate: cryst. from hot aq., m.p. 62° (2). [From  $\bar{C}$  slowly added to 10% aq. NH<sub>4</sub>OH (2 moles) (violent reactn. and cooling is required), yield 71% (2).]

- ④  $\gamma$ -Chloro-*n*-propyl allophanate ( $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{OCO.NH.CO.NH}_2$ ): cryst. from hot alc., m.p.  $166^\circ$  (2). [From  $\bar{\text{C}}$  with urea (2 moles) fused for 3 hrs. (75% yield (2)).]
- $\gamma$ -Chloro-*n*-propyl *N*-phenylcarbamate: pr. from alc., m.p.  $38^\circ$  (2),  $35\text{--}36^\circ$  (1). [From  $\bar{\text{C}}$  with aniline (2 moles) both diluted with dry ether (3 vols.) slowly mixed in flask surrounded by ice water, ether evaporated and prod. distilled, b.p.  $160\text{--}170^\circ$  at 5 mm. (2); this prod. in alc. on addn. of 1 *N* aq. NaOH ring-closes with loss of HCl giving (84% yield (2)) (1) 3-phenyl-tetrahydro-2-keto-1,3-oxazine, m.p.  $96^\circ$  (2),  $94.0\text{--}94.5^\circ$  (1).]
- ⑤  $\gamma$ -Chloro-*n*-propyl *N*-(*o*-tolyl)carbamate: ndls. from alc., m.p.  $49^\circ$  (2),  $46.0\text{--}46.5^\circ$  (1). [From  $\bar{\text{C}}$  with *o*-toluidine in dry ether as for preceding case (69% yield (2)); this prod. in alc. on addn. of 1 *N* aq. NaOH ring-closes with loss of HCl giving (60% yield (2)) (1) 3-(*o*-tolyl)-tetrahydro-2-keto-1,3-oxazine, m.p.  $89^\circ$  (1),  $87.0\text{--}87.5^\circ$  (2).]
- $\gamma$ -Chloro-*n*-propyl *N*-(*p*-tolyl)carbamate: oil, b.p.  $188^\circ$  at 4.5 mm.,  $D_4^{20} = 1.186$ ,  $n_D^{18} = 1.494$  (1). [This prod. with alc. KOH (1 mole) refluxed 2 hrs. ring-closes with loss of HCl giving (1) 3-(*p*-tolyl)-tetrahydro-2-keto-1,3-dioxazine, m.p.  $127.5\text{--}128^\circ$  (1).]
- ⑥  $\gamma$ -Chloro-*n*-propyl *N*-( $\alpha$ -naphthyl)carbamate: ndls. from ether and lgr., m.p.  $75.5\text{--}76.5^\circ$  (1). [From  $\bar{\text{C}}$  with  $\alpha$ -naphthylamine (2 moles) in aq. suspension (90% yield (1)); this prod. with alc. KOH (1 mole) refluxed 2 hrs. ring-closes with loss of HCl giving 3-( $\alpha$ -naphthyl)-tetrahydro-2-keto-1,3-dioxazine, m.p.  $149.5\text{--}150.5^\circ$  (1).]
- ⑦  $\gamma$ -Chloro-*n*-propyl *N'*-anilino-carbamate ( $\gamma$ -chloro-*n*-propyl *N*-phenylcarbazate): cryst. from  $\text{C}_6\text{H}_6$ , m.p.  $72^\circ$  (7). [From  $\bar{\text{C}}$  with phenylhydrazine (1 mole) in aqueous pyridine (62% yield (7)).]

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### 3:6025 $\beta,\beta'$ -DICHLORODIETHYL ETHER

(bis-( $\beta$ -chloroethyl) ether;  
"chlorox")



B.P.  $177\text{--}178^\circ$  cor. (1) M.P.  $-24.5^\circ$  (2)  $D_4^{20} = 1.2095$  (3)  $n_D^{20} = 1.457$  (1)  
 $176^\circ$  at 744 mm. (2)  
 $80\text{--}82^\circ$  at 20-22 mm. (3)  $D_4^{20} = 1.213$  (1)  
 $70^\circ$  at 15 mm. (2)  
 $66^\circ$  at 12 mm. (2)

Colorless oil with pleasant ethereal odor. — (For data on surface tension and parachor see (4); for vapor-press. data see (5).)

[For prepn. from ethylene chlorohydrin (3:5552) see (1); for use in prepn. of di-( $\beta$ -chloroethyl) sulfate see (12).] [Note that  $\bar{\text{C}}$  forms with ethylene chlorohydrin (3:5552) a const.-boil. mixt., b.p.  $128.2^\circ$ , contg. 8.2 mole %  $\bar{\text{C}}$  (15).]

The halogen atoms of  $\bar{\text{C}}$  are very unreactive to most reagents;  $\bar{\text{C}}$  is extremely resistant to hydrolysis, gives no Fiedel-Crafts reaction with  $\text{C}_6\text{H}_6 + \text{AlCl}_3$ , no reaction with KCN, and is unaffected by  $\text{NaOH} + \text{As}_2\text{O}_3$  (2).

$\bar{\text{C}}$  on hfg. with solid KOH yields (6) (7) (9) (3) divinyl ether (1:7800) (accompanied by some  $\beta$ -chloroethyl vinyl ether (3:7464) q.v.), but  $\bar{\text{C}}$  on hfg. with dimethylaniline or quinoline fails to react at all, even to form quaternary salt- (6).

$\bar{C}$  on htg. with excess sodium alcoholates for 3-15 hrs. gives 30-45% yields of the corresponding liquid bis ethers (8);  $\bar{C}$  in alc. refluxed overnight with an excess of Na phenolates yields corresponding bis ethers (9); e.g.,  $\bar{C}$  with Na  $\alpha$ -naphtholate gives 52% yield bis [ $\beta$ -( $\alpha$ -naphthoxy)ethyl] ether, m.p. 87° (9);  $\bar{C}$  with Na  $\beta$ -naphtholate gives 59% yield bis [ $\beta$ -( $\beta$ -naphthoxy)ethyl] ether, m.p. 122° (9).

$\bar{C}$  on htg. with aniline (3 moles) for 2 hrs. at 200° gives (95% yield (9)) 4-phenylmorpholine, white flakes from 50% alc., m.p. 57-58° (1). [The crude prod. may also cont. bis-( $\beta$ -anilinoethyl) ether, pl. from alc., m.p. 115.5° (9).] [For similar prepn. (77% yield (9)) of *N*-(*p*-tolyl)morpholine, m.p. 51° (8); *N*-( $\alpha$ -naphthyl)morpholine (98% yield (9)), m.p. 83° (8); *N*-( $\beta$ -naphthyl)morpholine (72% yield (9)), m.p. 90° (8), see (8) (9).] [For corresp. reaction of  $\bar{C}$  with phenylhydrazine, *p*-phenylenediamine, and benzidine see (10); with ethylenediamine see (11).]

—  $\beta, \beta'$ -bis-( $\alpha$ -Naphthoxy)diethyl ether: m.p. 87° (16). [From  $\bar{C}$  +  $\alpha$ -naphthol (1:1500) + aq. NaOH in a.t. at 120° for 8 hrs. (16).]

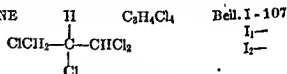
—  $\beta, \beta'$ -bis-( $\beta$ -Naphthoxy)diethyl ether: m.p. 122° (16). [From  $\bar{C}$  +  $\beta$ -naphthol (1:1540) + aq. NaOH in a.t. at 120° for 8 hrs. (16).]

⑨ bis-( $\beta$ -Phthalimidoethyl) ether [Beil. XXI-470]: from  $\bar{C}$  on refluxing 3 hrs. with phthalimide +  $K_2CO_3$  (13) or from  $\bar{C}$  + K phthalimide (2 moles) + trace of diethylamine on htg. 4 hrs. at 135-140° (55% yield) (9), cryst. from alc. (14), ndls. from 50% AcOH (13), m.p. 159° (9), 157° (13), 156.5° (14). [The half reaction prod.,  $\beta$ -chloro- $\beta'$ -phthalimidodiethyl ether, ndls. from lt. pet., m.p. 72° (13), 90° (9), may be sepd. from the above bis-ether by its much greater solubility in pet. eth. (13).]

3:6025 (1) Kamm, Waldo, *J. Am. Chem. Soc.* 43, 2223-2227 (1921). (2) Gibson, Johnson, *J. Chem. Soc.* 1930, 2525-2530. (3) Gulyaeva, Dauguleva, Caoutchouc and Rubber (U.S.S.R.) 1977 No. 1, 40-50, Cent. 1977 I 159 C 22 2750 (1977). (4) Gallagher, Hibbert, *J. Am. Chem. Soc.* 59, 2523 (1937). (5) Lott, Smith, Christiansen, *J. Am. J. Am. Chem. Soc.* 47, 163-166 47, 1173-1177 (1925) (16) Are.

(11) Hultquist, Northey, *J. Am. Chem. Soc.* 62, 447-448 (1940). (12) Suter, Evans, *J. Am. Chem. Soc.* 60, 536-537 (1938). (13) Baldwin, Robinson, *J. Chem. Soc.* 1934, 1266. (14) Gabriel, *Ber.* 38, 3413 (1905). (15) Snyder, Gilbert, *Ind. Eng. Chem.* 31, 1510-1521 (1912). (16) Dahlen, Black, Foohey (to du Pont Co), U.S. 1,979,144, Oct. 30, 1934; Cent. 1935, I 3051; [C.A. 29, 177 (1935)].

### 3:0035 1,1,2,3-TETRACHLOROPROPANE



B.P. 170-180° cor. at 756.6 mm. (1)  
170° (3)

$D_{15}^{20} = 1.522$  (1)

[For prepn. of  $\bar{C}$  from 1,2,3-trichloropropane (3:5840) +  $\text{ShCl}_5$  at 150-190° see (2); from 1,1,2-trichloropropane (3:5630) +  $\text{Cl}_2$  +  $\text{AlCl}_3$  s. (3:5280) +  $\text{Cl}_2$  see (4); from 3,3-dichloropropene-1 (3:1212) +  $\text{Cl}_2$  see (5); from 1,2-dichloroethylene (8:5030) with  $\text{CH}_2\text{Cl}_2$  (3:5020) + see (5).]

3:6035 (1) Romburgh, *Bull. soc. chim.* (2) 36, 553-557 (1881). (2) Herzfelder, *Ber.* 26, 2435 (1893). (3) Mounierat, *Bull. soc. chim.* (3) 21, 621-623 (1899). (4) Hartenstein, *J. prakt. Chem.* (2) 7, 312-313 (1873). (5) Lehmann, Bayer (to I.G.), *Ger.* 715,069, Dec. 10, 1911; Cent. 1912, I 2581; C.A. 38, 2051 (1914).

3:6050 1,1,3,3-TETRACHLOROPROPANONE-2  $\text{C}_3\text{H}_2\text{OCl}_4$  Beil. I - 656  
 (sym.-Tetrachloroacetone)  $\text{Cl}_2\text{CH}-\text{C}(=\text{O})-\text{CHCl}_2$  I<sub>1</sub>-(345)  
 I<sub>2</sub>—

B.P. 180-182° cor. at 718 mm. (1)  
 179-181° (3)

[See also 1,1,1,3-tetrachloropropanone-2 (unsym.-tetrachloroacetone) (3:6035).]

Colorless liq. with penetrating odor; produces blisters on skin. — Eas. sol. cold aq., alc., ether,  $\text{C}_6\text{H}_6$ .

$\bar{\text{C}}$  with aq. readily yields a crystn. tetrahydrate, m.p. 48-49° (1) (6), 48° (2), 47-48° (3) (4) (for crystallographic data see (2), for polymorphism see (5)); this tetrahydrate loses its aq. on distn., on stdg. over  $\text{H}_2\text{SO}_4$ , or by actn. of dry  $\text{HCl}$  gas.

[For prepn. of  $\bar{\text{C}}$  from phloroglucinol (1:1620) via conversion in  $\text{AcOH}$  with  $\text{Cl}_2$  to 1,1,3,3,5,5-hexachloro-2,4,6-triketocyclohexane ("hexachlorophloroglucinol") (Beil. VII-854, VII-469)], and treatment of latter with water (yield is almost quant.) (dichloroacetic acid (3:6203) is also formed) see (6); from 2,4,6-triaminophenol (Beil. XIII-569, XIII-(211)) (2), from chloroanilic acid (3:4970) (1) (7), from 3,3,5-trichlorocyclopentanetrione-1,2,4 (Beil. VII-852) (4), or from 2,2,5-trichlorocyclopentanedione-3,4-ol-1-carboxylic acid-1 (Beil. X-985) (4) by oxidn. with  $\text{KClO}_3 + \text{HCl}$  (other by-products are also formed and yield is low, e.g., 7% (7)) see indic. refs.; for formn. of  $\bar{\text{C}}$  from isopropyl alc. (1:6135) with  $\text{Cl}_2$  (8), from chloroacetone (3:5425) with  $\text{Cl}_2$  at 50-70° in light (9), or from 1,1-dibromo-3,3-dichloropropanone-2 (Beil. I-658) with alc.  $\text{HgCl}_2$  in s.t. at 100° for several hours (3) see indic. refs.]

[ $\bar{\text{C}}$  (as tetrahydrate) nn reduction with  $\text{Zn} + \text{H}_2\text{SO}_4$  yields (1) acetone (1:5400);  $\bar{\text{C}}$  on reduction with  $\text{Al}(\text{OEt})_3$ ,  $\text{Mg}(\text{OEt})_2$ , or  $\text{EtOMgCl}$  yields (10) 1,1,3,3-tetrachloropropanol-2 (3:9037).]

$\bar{\text{C}}$  with satd. aq.  $\text{NaHSO}_3$  readily yields a  $\text{NaHSO}_3$  cpd. (3).

$\bar{\text{C}}$  with aq. alk. does not (3) yield chloroform;  $\bar{\text{C}}$  with alk. + aniline does not (3) give phenylisocyanide (carbylamine test). [Dif. from the isomeric unsym.-tetrachloroacetone (3:6035).]

$\bar{\text{C}}$  in abs. ether with dry  $\text{NH}_3$  gas adds 1  $\text{NH}_3$  giving (92% yield (2)) 1,1,3,3-tetrachloro-2-aminopropanol-2 (Beil. I-656), ndls. from  $\text{C}_6\text{H}_6$ , m.p. 110-111° dec. with prev. sublimation; this prod. is eas. sol. in cold aq. but on warming the soln. dissociates into its components. — [The action of  $\bar{\text{C}}$  with aq.  $\text{NH}_4\text{OH}$  or with aniline has not been clarified cf. (3).]

[ $\bar{\text{C}}$  with excess conc. aq.  $\text{HCN}$  warmed at 50-60° soon dissolves and after 12 hrs. warming (2) ppts.  $\beta,\beta,\beta',\beta'$ -tetrachloro- $\alpha$ -hydroxyisobutyronitrile (Beil. III-318), cryst. from  $\text{C}_6\text{H}_6$ , m.p. 112-114° (2); this prod. with  $\text{AcOH}/\text{H}_2\text{SO}_4$  as directed (2) yields the corresp.  $\beta,\beta,\beta',\beta'$ -tetrachloro- $\alpha$ -hydroxyisobutyramide, cryst. from  $\text{C}_6\text{H}_6$ , m.p. 156° (2).]

$\bar{\text{C}}$  with  $\text{PCl}_5$  on htg. gives (2) mainly 1,1,2,2,3,3-hexachloropropane (3:6075) accompanied by some 1,1,2,3,3-pentachloropropene-1 (3:6075).

[ $\bar{\text{C}}$  with diazotized aniline (4 moles) in pres. of  $\text{NaOAc}$  yields (11) dichloro-bis-(benzeneazo)methane, yel.-or. cryst. from hot alc., m.p. 81-82° (11);  $\bar{\text{C}}$  with diazotized *p*-toluidine (4 moles) in pres. of  $\text{NaOAc}$  yields (11) dichloro-bis-(*p*-tolueneazo)methane, orange cryst. from  $\text{C}_6\text{H}_6$ , m.p. 159-160° (11).] [These prods. are also similarly obt'd. (11) from unsym.-dichloroacetone (3:6035).]

④ 4-(Benzeneazo)-1-phenylpyrazole (Beil. XXV-535): golden-yel. lfts. from dil. alc. or lgr., ndls. from  $\text{AcOH}$ , m.p. 126-127° cor. (2), 126° (6). [From  $\bar{\text{C}}$  in abs. alc. (2) or  $\text{AcOH}$  (6) with excess phenylhydrazine, refluxed for 5 min.]



3:6050 (1) Levy, Jedlicka, *Ann.* **249**, 89-95 (1888). (2) Levy, Curchod, *Ann.* **252**, 330-349 (1889). (3) Cloëz, *Ann. chim.* (6) **9**, 182-186 (1886). (4) Hantzsch, *Ber.* **21**, 2438 (1888). (5) Schaum, Schalling, Klausung, *Ann.* **411**, 192 (1916). (6) Zincke, Kegel, *Ber.* **22**, 1467-1477; 1478-1482 (1889). (7) Levy, Witte, *Ann.* **254**, 86-88 (1889). (8) Buc (to Standard Oil Co.), U.S. 1,391,757, Sept. 27, 1921; *Cent.* **1922**, IV 942. (9) I.G., French 816,956, Aug. 21, 1937; *Cent.* **1938**, I 2216. (10) Meerwein, von Bock, Kirschnick, Lenz, Migge, *J. prakt. Chem.* (2) **147**, 212, 225 (1936).

(11) Favrel, *Bull. soc. chim* (5) **1**, 988-989 (1931).

3:6055 *o*-DICHLOROBENZENE

Beil. V - 201

V<sub>1</sub>-(111)V<sub>2</sub>-(153)

B.P.

F.P.

180.3°	at 760 mm.	(1)	-16.7° (1)	$D_4^{25} = 1.2965$ (3)	
180.3°	at 760 mm.	(2)	-17.1° (2) (11)	1.2934 (13)	
180.2°	at 757.4 mm.	(1)	-17.5° (10)	$n_D^{25} = 1.5486$	(2)
			(12) (15)	1.5476	(13)
179-181°	at 755 mm.	(3)		$n_D^{22} = 1.5518$	(1)
179.9-180.6°		(4)	-17.6° (10)	$D_4^{20} = 1.3048$ (12)	
179.5-180.5°		(5)	-18° (8a)	1.299 (14)	
179.5°	at 746.2 mm.	(1)		$n_D^{20} = 1.5513$	(2)
178.7-179.5°		(6)		1.549	(14)
179°	cor.	(7)		$n_D^{17} = 1.5532$	(10)
178°	at 762.5 mm.	(8)		1.5524	(12)
178°	at 768 mm.	(8a)		$D_4^{15} = 1.3104$ (12)	
86°	at 18 mm.	(8)		1.3085 (14)	
85°	at 16 mm.	(9)		$n_D^{15} = 1.55293$	(14)
65.8°	at 14 mm.	(10)		$D_{20}^{20} = 1.3088$ (1)	
				$D_{15}^{15} = 1.3112$ (1)	

$\bar{C}$  when pure is colorless oil, volatile with steam. — Ord. comml.  $\bar{C}$  conts. also the isomeric *p*-dichlorobenzene (3:0980), even as much as 25% (16); and a comml. prod. sold as insecticide conts. 40%  $\bar{C}$  + 30% *p*-dichlorobenzene (3:0980) + 30% trichlorobenzene (17).

[For f.p./compn. data and diagram of system  $\bar{C}$  + *p*-dichlorobenzene (3:0980) (eutectic, m.p. -23.4°, contg. 86.7%  $\bar{C}$ ) see (10) (11); for f.p./compn. data and diagram of system  $\bar{C}$  + *m*-dichlorobenzene (3:5960) (eutectic, m.p. -45.9°, contg. 48.7%  $\bar{C}$ ) see (11); for f.p./compn. data on ternary system of all three dichlorobenzenes see (10).]

[For data on densities of solns. of  $\bar{C}$  in  $C_6H_6$  (1:6400) and in *n*-hexane (1:8530) see (18); for data on  $D_{20}^{20}$  and  $n_D^{20}$  on system  $\bar{C}$  + diethylbenzene (and use of the mixt. in testing fractionating columns) see (19).]

[ $\bar{C}$  is very spar. sol. aq. (for study of this soly. over range 20-60° see (20).]

[For study and use of  $\bar{C}$  as cleaner for metals see (21); for use as solvent for fats and oils (16) and for detn. of oils in acids (by use of density of resultant extract (22) see indic. refs.; for use for removal of tar or pitch from surfaces coated with cellulose esters see (23); for use as solv. in purification of anthraquinone see (24); for study of toxicity of  $\bar{C}$  see (25).]

[For prepn. of  $\bar{C}$  from *o*-chloroaniline [Beil. XII-597, XII<sub>1</sub>-(297)] via diazotization and use of  $Cu_2Cl_2$  reactn. (yields: 70% (26), 25% (27)) (1) (8) (28) see indic. refs.; from *o*-phenylenediamine [Beil. XIII-6, XIII<sub>1</sub>-(5)] via tetrazotization in AcOH with nitrosyl-sulfuric acid followed by use of  $Cu_2Cl_2$  reactn. (70.1% yield) see (29); from 1,2-dichlorobenzenesulfonic acid-4 (see below) by distn. from a strong  $H_2SO_4$  with superheated steam at 200-240° see (30).]

[For formn. of  $\bar{C}$  from 2-chlorophenol (3.5980) by htg. with  $PCl_5$  (20% yield) see (7); from *o*-bromonitrobenzene [Beil. V-247, V<sub>1</sub>-(131)] with  $PCl_5$  in s.t. at 180° (31) or with  $NH_4Cl$  in s.t. at 320° (32) see indic. refs., from *o*-dinitrobenzene [Beil. V-257, V<sub>1</sub>-(135)] with conc.  $HCl$  in s.t. at 250-270° see (33)]

[For formn. of  $\bar{C}$  (together with *m*- and *p*-isomers in some cases) from  $C_6H_6$  with  $Cl_2$  in pres. of  $I_2$  (7),  $AlCl_3$  (34) (35), or  $SnCl_4$  (36) see indic. refs., from chlorobenzene (3:7903) with  $Cl_2$  + cat. at 600° (11) cf. (37) or with  $Cl_2$  in pres. of  $Al/Hg$  (38),  $AlCl_3$  (gives 30%  $\bar{C}$  (11)) (34),  $FeCl_3$  (gives 39%  $\bar{C}$  (11)), or with  $Al_2S_2Cl_8$  (i.e.,  $2AlCl_3 + S_2Cl_2$ ) +  $SO_2Cl_2$  (38) see indic. refs.]

[ $\bar{C}$  with  $Cl_2$  in pres. of  $Al/Hg$  (38) or  $FeCl_3$  (39) (40) (41) gives mainly 1,2,4-trichlorobenzene (3:6420), but 1,2,3-trichlorobenzene (3:0990) is also formed (41). —  $\bar{C}$  with  $Cl_2$  in s.t. at room temp. in sunlight as directed (42) adds  $3Cl_2$  yielding *o*-dichlorobenzene-hexachloride, m.p. 149° (42).] — [For study of photochem. chlorination of  $\bar{C}$  see (43).]

[ $\bar{C}$  with  $Mg$  in dry ether does not react (44)] — [ $\bar{C}$  with  $CO$  + cat. at elev. temps. gives (45) benzoic acid, presumably through intermediate formn. of *o*-phthalic acid and subsequent loss of  $CO_2$ .]

[ $\bar{C}$  with isopropyl alc. (1.6135) +  $BF_3$  +  $P_2O_5$  under reflux gives (53% yield (87)) 3,4-dichloro-*isopropylbenzene* (3,4-dichloro-*isopropylbenzene*) (87)]

[ $\bar{C}$  with  $CH_2Cl$  (3.7005) +  $AlCl_3$  yields (30) hexamethylbenzene (1:7265) + *iso*-trichloromesitylene (3.8725). —  $\bar{C}$  (3+ moles) with  $CHCl_3$  (1 mole) +  $AlCl_3$  without solv. at 55° for 8 hrs. gives (15% yield on the  $CHCl_3$  (46)) *trans*-(3,4-dichlorophenyl)methane, white pl., m.p. 160.5-162° (46) —  $\bar{C}$  with  $CCl_4$  +  $AlCl_3$  presumably yields 3,4,3',4'-tetrachlorobenzophenone dichloride (not isolated) since the reaction prod. with 95% alc. (46) or  $AcOH/H_2SO_4$  (47) gives 3,4,3',4'-tetrachlorobenzophenone, cryst. from hot alc. or hot acetone, m.p. 141-142° (46), 142° (47) (accompanied in latter case ( $H_2SO_4$ ) by some 3,4-dichlorobenzoic acid (3.4925), m.p. 203° (47).]

[ $\bar{C}$  with acetyl  $Cl$  (3:7005) +  $AlCl_3$  gives (yields: 70% (49), 40% (48)) 3,4-dichloroacetophenone, b.p. 135° at 12 mm. (48), m.p. 76° (48), 74° (49) (corresp. oxime, m.p. 107° (50)). —  $\bar{C}$  with chloroacetyl chloride (3.5235) +  $AlCl_3$  gives (50) (85) 3,4-dichlorophenacyl chloride (3,4-*ω*-trichloroacetophenone), m.p. 43° (50), 44° (85). —  $\bar{C}$  with  $\beta$ -chloro-*n*-butyric acid (3:0035) +  $AlCl_3$  or conc.  $H_2SO_4$  yields (51) by condens. and subsequent ring closure a mixt. of *x,y*-dichloro-3-methylindanone-1 epids.]

[ $\bar{C}$  with phthalic anhydride (1:0725) +  $AlCl_3$  gives (yields: 80% (5), 73% (52) (53), 35% (54)) (55) *o*-(3,4-dichlorobenzoyl)benzoic acid, m.p. 194.5° cor. (54), 192.5° (5), 191.2° cor. (52), 190° (55), this prod. on ring closure with conc.  $H_2SO_4$  gives a mixt. of two dichloroanthraquinones consisting of 87% (54) (5) 2,3-dichloroanthraquinone [Beil. VII<sub>1</sub>-(413)], m.p. 271° cor. (54), 268° (5), and 13% (54) (5) 1,2-dichloroanthraquinone [Beil. VII<sub>1</sub>-(411)], m.p. 196.5° cor. (54), 194.5° (5). Note that  $\bar{C}$  reacts with phthalic anhydride much more readily than *p*-dichlorobenzene (3:0980), after making reactn. mixt. alk. any *p*-dichlorobenzene (as from use of crude  $\bar{C}$ ) may be distilled out with steam (use in sepn. of *p*-dichlorobenzene from  $\bar{C}$  (86)); note also the claim (86) that under certain conditions  $\bar{C}$  with phthalic anhydride +  $AlCl_3$  is claimed to replace 1 chlorine atom by hydrogen so that an *o*-(*x*-chlorobenzoyl)benzoic acid results which on ring closure with 100%  $H_2SO_4$  gives 80% yield 2-chloroanthraquinone (3:4922). —  $\bar{C}$  with 4,5-dichlorophthalic anhydride (3:4830) +  $AlCl_3$  gives (80% yield (56)) 2-(3,4-dichlorobenzoyl)4,5-dichlorobenzoic acid, cryst. from  $C_6H_6$ , m.p. 183° (56); this prod. with conc.  $H_2SO_4$  ring-closes giving mainly 2,3,6,7-tetrachloroanthraquinone, m.p. 318° (56), accompanied by a little 1,2,6,7-tetrachloroanthraquinone, m.p. 242° (56).]

[ $\bar{C}$  on partial hydrol. with aq.  $MeOH$  alk., alk. carbonates, or best alk. earths in pres. of  $Cu$  or  $Cu$  salts at elevated temps. under press. gives in excellent yields (57) (58) (59) (60)

(61) (62) (63) (64) (65) *o*-chlorophenol (3:5980) (some phenol (1:1420) is also formed (62)); if the hydrolysis of  $\bar{C}$  is carried further, especially by use of aq. alk. in pres. of Ba or Sr salts and a reducing agt. (66), pyrocatechol (1:1520) is obtd. cf. (59) (61) (64).] — [For study of kinetics of reactn. of  $\bar{C}$  with NaOMe/MeOH at 175° see (67) (68) (69).]

[ $\bar{C}$  with anhyd.  $NH_3$  in alc. in pres. of  $CuCl_2 + Cu$  at 200° under press. yields (70) *o*-chloroaniline;  $\bar{C}$  with conc. aq.  $NH_4OH$  in pres. of  $CuO$  under press. at 150–200° (71) (72) or with Na in liq.  $NH_3$  (73) gives *o*-phenylenediamine.] — [ $\bar{C}$  with K diphenylamine gives by rearr. on btg. (74) (75)  $N,N,N',N'$ -tetraphenyl-*m*-phenylenediamine [Beil. XIII-42], m.p. 137.5–138° (74) (75).]

[ $\bar{C}$  on mononitration, e.g., at 0° with a mixt. of  $HNO_3$  ( $D = 1.52$ ) + conc.  $H_2SO_4$  (75) cf. (15) (4), gives (yields: 95% (15), 67% (75)) (7) (8) (76) mainly 1,2-dichloro-4-nitrobenzene [Beil. V-246, V<sub>1</sub>-(131)], cryst. from alc., m.p. 43° (7) (8), 42.5° (4) (reactn. prod. with piperidine is 2-chloro-4-nitropiperidinobenzene, m.p. 47–48° (78)), accompanied by a little (5.2% at –30°, 7.2% at 0° (8)) 1,2-dichloro-4,5-dinitrobenzene (see below).] — [The only other possible mononitro-isomer, viz., 1,2-dichloro-3-nitrobenzene [Beil. V-245, V<sub>1</sub>-(130)], m.p. 61°, has been obtd. only by indirect means (77) (76) although prob. present (4) in the oil from the main mononitration product.]

[ $\bar{C}$  on dinitration, e.g., with 4 wt. pts.  $HNO_3$  ( $D = 1.52$ ) + 6 wt. pts. conc.  $H_2SO_4$  at 100° for 1 hr. (79) (28) cf. (80) (or the above 1,2-dichloro-4-nitrobenzene with  $HNO_3$  ( $D = 1.6$ ) + fuming  $H_2SO_4$  (20%  $SO_3$ ) 2 hrs. at 100° (78)), gives 1,2-dichloro-4,5-dinitrobenzene [Beil. V-265], cryst. from dil. AcOH, m.p. 109–110° (78), 110° (28) (79) (reactn. prod. with piperidine is 1,2-dichloro-4-nitro-5-piperidinobenzene, m.p. 62–64° (78)), accompanied (28) by a little 1,2-dichloro-3,5-dinitrobenzene [Beil. V<sub>1</sub>-(133)], m.p. 56° (28).] — [All the other possible isomeric *o*-dichlorodinitro cpds. are known but have been obtd. only by indirect means: 1,2-dichloro-3,4-dinitrobenzene [Beil. V-264], m.p. 53–55°, 1,2-dichloro-3,6-dinitrobenzene, m.p. 60°, and 1,2-dichloro-4,6-dinitrobenzene, m.p. 56°.]

[None of the four possible 1,2-dichloro-trinitrobenzenes appears to have been reported.]

[ $\bar{C}$  on monosulfonation, e.g., with fuming  $H_2SO_4$  in s.t. at 210° for 8 hrs. (7), or at room temp. (30), or at 100° (10), or with  $H_2SO_4 \cdot H_2O$  + fuming  $H_2SO_4$  (60%  $SO_3$ ) in pres. of Hg at 100° for 1 hr. (81), gives mainly 1,2-dichlorobenzenesulfonic acid-4 [Beil. XI-55, XI<sub>1</sub>-(16)] (Na salt less sol. aq. (81)) accompanied by a lesser amt. of 1,2-dichlorobenzenesulfonic acid-3 (Na salt more sol. aq. (81)) (some *bis*-(dichlorophenyl) sulfone, m.p. 173° (30), may also be formed during sulfonation).] — [ $\bar{C}$  sulfonates much more readily than *p*-dichlorobenzene (3:0980); for use in sepn. see (7) (30); for removal of chlorobenzene from mixt. with dichlorobenzenes via sulfonation of former with 95%  $H_2SO_4$  see (11).]

① 1,2-Dichlorobenzenesulfonamide-4 (3,4-dichlorobenzenesulfonamide-1): cryst. from dil. alc., m.p. 134–135° u.c. (83). [From  $\bar{C}$  by treatment as directed (83) with  $ClSO_3H$  followed by conv. of the intermediate 1,2-dichlorobenzenesulfonyl chloride-4, m.p. 18–19° (83), with  $(NH_4)_2CO_3$  to the desired sulfonamide.] — [For formn. of 3,4-dichlorobenzenesulfonyl chloride with  $ClSO_3H$  and use in sepn. of  $\bar{C}$  from *p*-dichlorobenzene see (82); for prepn. of the sulfonamide and use as plasticizer see (84).]

nyth, *J. Am. Chem. Soc.* 64,  
thoff, *J. Am. Chem. Soc.* 55,  
1-1033 (1933). {6} Dadiou,  
urbatow, *Ann.* 176, 40–43  
or, *Z. physik. Chem.*  
334 (1911).  
2) Narbutt, *Ber.* 52,  
} von Auwers, *Ann.*  
–3041 (1928). {16}

(1875); 182, 94–95 (1876). {8} Holleman, Reiding, *Rec. trav. chim.* 23, 358–359, 370–379 (1904).



3:6060 *d,l*-2,3-DICHLOROPROPANOL-1  $\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{H}-\text{C}-\text{Cl} \\ | \\ \text{CH}_2\text{OH} \end{array}$   $\text{C}_3\text{H}_5\text{OCl}_2$  Beil. I - 356  
(Glycerol  $\alpha,\beta$ -dichlorohydrin;  
"  $\beta$ -dichlorohydrin "; allyl  $\text{I}_1$ -(181)  
alcohol dichloride)  $\text{I}_2$ -(370)

B.P.  $182^\circ$  at 760 mm. (1)  $D_4^{20} = 1.3534$  (5)  
 $182^\circ$  (2) (3) (8)  
 $179-181^\circ$  sl. dec. (4)  $D_0^{18} = 1.345$  (4)  $n_D^{18} = 1.4875$  (4)  
 $79-80.5^\circ$  at 18 mm. (4)  
 $81-81.5^\circ$  at 13.5 mm. (5)  
 $75-77^\circ$  at 15 mm. (6)

Colorless visc. liq.; spar. sol. cold aq., pet. ether; misc. with alc., ether, acetone,  $\text{C}_6\text{H}_6$ .

[For prepn. of  $\bar{\text{C}}$  from glycerol (1:6540) (together with other prods.) see (1); for prepn. from allyl alcohol (1:6145) with  $\text{Cl}_2 + \text{aq.}$  (2) (7) (8) (5) (20% yield) or with  $\text{Cl}_2$  in  $\text{CS}_2$  (40% yield (9)) see indic. refs.; from allyl chloride (3:7035) by addition of  $\text{HOCl}$  see (10) (11) (12); from the corresp. acetate ( $\beta,\gamma$ -dichloro-*n*-propyl acetate) (3:6220) by alcoholysis using  $\text{MeOH} + \text{HCl}$  (33% yield (4)) (6); from vinyl chloride (3:7004) by reactn. with formaldehyde (30% soln.) +  $\text{HCl} + \text{CaCl}_2$  see (13).]

$\bar{\text{C}}$  with aq. alk. loses  $\text{HCl}$  yielding (14) 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358). [For studies of kinetics of this loss of  $\text{HCl}$  with aq. alk. see (15); for use of  $\text{Ba}(\text{OH})_2$  hydrol. as means of detn. of  $\bar{\text{C}}$  in pres. of 1,3-dichloropropanol-2 ("  $\alpha$ -dichlorohydrin ") (3:5985) see (16) ]

$\bar{\text{C}}$  with sodium phenolate does *not* give the expected 2,3-diphenoxypropanol-1 but instead (4) (presumably by intermediate formation of epichlorohydrin (3:5358)) the isomeric 1,3-diphenoxypropanol-2, [Beil. VI-149, VI-1-(86)], m.p.  $79^\circ$  (4).

$\bar{\text{C}}$  on oxidn. with conc.  $\text{HNO}_3$  ( $D = 1.47$ ) yields (12) (17) (6) (18)  $\alpha,\beta$ -dichloropropionic acid (3:0855), m.p.  $50^\circ$ . [ $\bar{\text{C}}$  on reductn. with  $\text{P} + \text{HI}$  at  $180^\circ$  yields (8) isopropyl iodide + isopropyl chloride.]

[ $\bar{\text{C}}$  with  $\text{SOCl}_2$  at  $100^\circ$  gives (85% yield (19)) bis-( $\beta,\gamma$ -dichloro-*n*-propyl) sulfite, h.p.  $175^\circ$  at 4 mm.,  $D_0^{23.7} = 1.501$ ,  $n_D^{23} = 1.509$  (19);  $\bar{\text{C}}$  with  $\text{SO}_2\text{Cl}_2$  gives (75% yield (19)) 2,3-dichloropropane-sulfonyl chloride-1, b.p.  $122-123^\circ$  at 15 mm.,  $D_0^{20.5} = 1.582$ ,  $n_D^{23} = 1.457$  (19).]

[ $\bar{\text{C}}$  with  $\text{PCl}_5$  yields (7) 1,2,3-trichloropropane (3:5840);  $\bar{\text{C}}$  with  $\text{NaCN}$  gives (20) (presumably by formation and subsequent reaction of epichlorohydrin) 25% yield  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-butyronitrile; for reactn. of  $\bar{\text{C}}$  with  $\text{NH}_3$  see (21); for reactn. of  $\bar{\text{C}}$  with  $\text{Na}_2\text{S}$ ,  $\text{NaSH}$ , etc., yielding thioglycerols see (22).]

—  $\beta,\gamma$ -Dichloro-*n*-propyl acetate: b.p.  $192^\circ$  (see 3:6220). [For general study of kinetics of esterification of  $\bar{\text{C}}$  see (3).]

—  $\beta,\gamma$ -Dichloro-*n*-propyl benzoate: oil, b.p.  $180-183^\circ$  at 24 mm. (4).

Ⓓ  $\beta,\gamma$ -Dichloro-*n*-propyl *p*-nitrobenzoate: m.p.  $37-38^\circ$  (4),  $35.5-37^\circ$  (23). [From  $\bar{\text{C}}$  + *p*-nitrobenzoyl chloride + pyridine (23).]

—  $\beta,\gamma$ -Dichloro-*n*-propyl 3,5-dinitrobenzoate: unreported.

—  $\beta,\gamma$ -Dichloro-*n*-propyl benzenesulfonate: unreported.

—  $\beta,\gamma$ -Dichloro-*n*-propyl *p*-toluenesulfonate: unreported.

Ⓓ  $\beta,\gamma$ -Dichloro-*n*-propyl *N*-phenylcarbamate: cryst. from lgr., m.p.  $72-73^\circ$  (24),  $73-74^\circ$  (25). [From  $\bar{\text{C}}$  + phenyl isocyanate at  $90^\circ$  (24) or indirectly from  $\beta,\gamma$ -dichloro-*n*-propyl chloroformate with aniline (25).]

Ⓓ  $\beta,\gamma$ -Dichloro-*n*-propyl *N*-( $\alpha$ -naphthyl)carbamate: ndls. from alc., m.p.  $93^\circ$  (25).

[Prepd. indirectly from  $\beta,\gamma$ -dichloro-*n*-propyl chloroformate with  $\alpha$ -naphthylamine (25).]

- ⑤  $\beta,\gamma$ -Dichloro-*n*-propyl *N*-( $\beta$ -naphthyl)carbamate: lfts. from alc., m.p. 99° (25).  
[Prepd. indirectly from  $\beta,\gamma$ -dichloro-*n*-propyl chloroformate with  $\beta$ -naphthylamine (25).]

3:6060 (1) Gibson, *J. Soc. Chem. Ind.* 50, 949-954; 970-975 (1931). (2) Tollens, *Ann.* 156, 161-166 (1870). (3) Kailan, Rosenblatt, *Monatsh.* 68, 109-170 (1936). (4) Delaby, Dubois, *Bull. soc. chim.* (4) 47, 572-573 (1930). (5) Read, Hurst, *J. Chem. Soc.* 121, 989-999 (1922). (6) Bockemüller, Hoffmann, *Ann.* 519, 189-190 (1935). (7) Hubner, Müller, *Ann.* 159, 179-183 (1871). (8) Torneø, *Ber.* 24, 2672 (1891). (9) King, Pyman, *J. Chem. Soc.* 105, 1257 (1914). (10) von Gegerfelt, *Ann.* 154, 247-249 (1870); *Ber.* 6, 720-721 (1873).

(11) Henry, *Ber.* 3, 352 (1870). (12) Henry, *Ber.* 7, 414 (1874). (13) I.G., *Brit.* 465,467, May 3, 1937, *Cent.* 1937, II 1445, *C.A.* 31, 7067, French 812,292, May 4, 1937; *Cent.* 1937, II 1445; *C.A.* 32, 952 (1938). (14) Münder, Tollens, *Zeit. für Chemie* 1874, 252. (15) Smith, *Z. physik. Chem.* 92, 739-740 (1917); 93, 83-85 (1919). (16) Smith, *Z. physik. Chem.* 95, 83-88 (1920). (17) Werigo, Melikoff, *Ber.* 10, 1499-1500 (1877). (18) Koelsch, *J. Am. Chem. Soc.* 52, 3365 (1930). (19) Levaillant, *Compt. rend.* 197, 335-337 (1933). (20) Braun, *J. Am. Chem. Soc.* 52, 3170 (1930).

(21) Lillienfeld, *Brit.* 390,516, *Brit.* 390,523, May 4, 1933; French 739,699, Jan. 16, 1933; *Cent.* 1933, II 1443. (22) Lillienfeld, *Brit.* 385,980, Feb. 2, 1933, *Cent.* 1933, II 1928; French 758,359, Jan. 15, 1934; *Cent.* 1934, I 3653. (23) Conant, Quayle, *J. Am. Chem. Soc.* 45, 2772 (1923). (24) Johnson, Langley, *Am. Chem. J.* 44, 360 (1910). (25) Otto, *J. prakt. Chem.* (2) 44, 21-22 (1891).

3:6075 1,1,2,3,3-PENTACHLOROPROPENE-1  $\text{Cl}$   $\text{C}_2\text{HCl}_3$  *Beil. I* - 200  
 $\text{Cl}_2\text{C}=\text{CCHCl}_2$   $I_1-(83)$   
 $I_2-$   
 B.P. 183° (1)  $D_4^{25} = 1.6317$  (1)  $n_D^{20} = 1.5313$  (1)  
 116° at 9 mm. (1)

$\text{C} + \text{Br}_2$  in sunlight gives (1) 1,2-dibromo-1,1,2,3,3-pentachloropropane, m.p. 71° (1).

$\text{C}$  with powdered KOH in toluene at 100° yields (1) a prod.  $\text{C}_4\text{Cl}_8$ , colorless ndls., m.p. 93-94° (1).

$\text{C}$  shaken with conc.  $\text{H}_2\text{SO}_4$ , poured onto ice, yields 2,3,3-trichloropropen-2-ol-1 ( $\alpha,\beta$ -trichloroacrolein) [*Beil. I*-(378)], b.p. 164° (1), m.p. 30° (1). [Oxime, m.p. 101°, converted on fusion into stereoisomer, m.p. 132° (1); phenylhydrazone, yel.-hr. ndls., m.p. 97-98° dec. (1).]

$\text{C}$  with conc.  $\text{H}_2\text{SO}_4$  for a longer time at 40-50°, poured onto ice, ppts. (1)  $\alpha,\beta$ -dichloroacrylic ac. (3.2265), m.p. 86° (1)

3:6075 (1) Prins, *J. prakt. Chem.* (2) 89, 419-420 (1914).

3:6085 1,1,1,3-TETRACHLOROPROPANONE-2  $\text{C}_2\text{H}_2\text{OCl}_4$  *Beil. I* - 656  
 (unsym.-Tetrachloroacetone)  $\text{CH}_2-\text{C}-\text{CCl}_3$   $I_1-$   
 $\text{Cl}$   $\text{O}$   $I_2-$   
 B.P. 183° (1)  $D_4^{25} = 1.624$  (1)  $n_D^{25} = 1.497$  (1)  
 180-182° (2)  
 71-72° at 13 mm. (3)

[See also 1,1,3,3-tetrachloropropanone-2 (3:6050).]

Colorless hmpid liq.; odor faint by itself but on warming or on dilution with ether shows

lachrymatory props. —  $\bar{C}$  with aq. readily yields (1) (2) (3) (4) a crystn. tetrahydrate, m.p. 40° (1), 39° (2), 65° (3).

[For prepn. of  $\bar{C}$  from isopropyl alc. (propanol-2) (1:5135) with  $Cl_2$  in cold see (1); from acetone (1:5400) with  $Cl_2$  see (2) (4) (5); from chloroacetone (3:5425) with  $Cl_2$  at 50-70° in light see (6); from 1,1,1-trichloropropanone-2 (3:5620) with  $SOCl_2$  at 180° see (3).]

$\bar{C}$  reduces  $NH_4OH/AgNO_3$ , Fehling's soln., or aq.  $KMnO_4$  instantly in cold (1) but does not give fuchsin-aldehyde test (1).

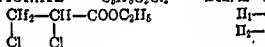
$\bar{C}$  with  $NH_4OH$  (1) yields chloroform (3:5050) and chloroacetamide [Beil. II-109, II<sub>1</sub>-(90), II<sub>2</sub>-(103)], m.p. 110-117°.

$\bar{C}$  with aq.  $KOH$  yields (1) chloroform (3:5050) together with the salts of both chloroacetic acid (3:1370) and trichloroacetic acid (3:1150). [Dif. from the isomeric *sym.*-tetrachloroacetone (3:0050).]

$\bar{C}$  with aq.  $KOH$  + aniline yields (5) phenyl isocyanido (carbylamino reaction). [Dif. from the isomeric *sym.*-tetrachloroacetone (3:5050).]

3:6085 (1) Brochet, *Bull. soc. chim.* (3) 13, 117-120 (1895); *Ann. chim.* (7) 10, 134-141 (1897); *Compt. rend.* 110, 1271 (1894). (2) Ciożz, *Ann. chim.* (6) 9, 180-182 (1888). (3) Arndt, Amende, Ender, *Monatsh.* 50, 215 (1932). (4) Bouis, *Ann.* 64, 316-319 (1848). (5) Bischoff, *Ber.* 8, 1349-1341 (1875). (6) I.G., French 816,956, Aug. 21, 1937; *Cent.* 1938, I 2210.

3:6090 ETHYL *d,l*- $\alpha,\beta$ -DICHLOROPROPIONATE  $C_5H_8O_2Cl_2$  Beil. II - 252



B.P. 183-184° (1)

182-185° (3)

70-77° at 15 mm. (2)

$D_4^{20} = 1.2461$  (3)

$n_D^{20} = 1.44815$  (3)

[For prepn. of  $\bar{C}$  from  $\alpha,\beta$ -dichloropropionic acid (3:0855) with abs. EtOH + dry HCl at 0° (74-78% yield (2)) (1) see indic. refs.; from  $\alpha,\beta$ -dichloropropionyl chloride (3:0034) with EtOH see (4) (3) (5).]

$\bar{C}$  is difficult to keep and readily loses HCl (3). —  $\bar{C}$  on htg. with dimethylaniline, quinoline, or quinaldine at 100° for 10 min. under  $N_2$  loses HCl yielding (4) ethyl  $\alpha$ -chloroacrylate (3:0242).

$\bar{C}$  with  $Ba(OH)_2$  both saponifies and loses HCl yielding (5) (6)  $\alpha$ -chloroacrylic acid (3:1445), m.p. 65°.

$\bar{C}$  reacts easily with alc. KCN, and after boilg. the resulting soln. with KOH yields (7) fumaric acid (1:0895) and *d,l*-malic acid.

$\bar{C}$  on boilg. with 20% HCl hydrolyzes (4) yielding EtOH (1:0130) and  $\alpha,\beta$ -dichloropropionic acid (3:0855) q.v.

3:6090 (1) Werigo, Melikov, *Ber.* 10, 1500 (1877). (2) Yarnall, Wallis, *J. Org. Chem.* 4, 287 (1939). (3) Brühl, *Ann.* 203, 25 (1880). (4) Marvel, Dec, Cooke, Cowan, *J. Am. Chem. Soc.* 62, 3495-3498 (1940). (5) Werigo, Werner, *Ann.* 170, 167 (1873). (6) Otto, Beckurts, *Ber.* 18, 243 (1885). (7) Werigo, Tanatar, *Ann.* 174, 367-372 (1874).

e (1) (10) (5) (6) (11); from  $\alpha,\beta,\beta$ -trichlorodietbyl ether + Zn (78% yield (4)), (3), or NaOEt (12), or even water (3); from  $\alpha,\beta,\beta,\beta$ -tetrachlorodiethyl ether abs. alc (13).]

rmg. with conc.  $H_2SO_4$  (14) (2) or on btg. at  $150^\circ$  with conc. HCl (15) or on htg. ic anhydride + a little conc.  $H_2SO_4$  gives (yield 81% (1), 78% (10), 71% (16)) etaldehyde (3:5180), b.p.  $90-91^\circ$ .

g. with alc. NaOH at  $160-180^\circ$  yields (17) glyoxal tetraetbylacetal [Beil. I-760], (17). —  $\bar{C}$  with K *ter*-butylate loses HCl yielding (5) chloroketene dietbylacetal, at 732-740 mm.,  $D_{15}^{25} = 1.0534$ ,  $n_D^{25} = 1.4375$  (5).

$PCl_5$  yields (15)  $\alpha,\beta,\beta$ -trichlorodiethyl ether [Beil. I-615].

van de Walle, *Bull. soc. chim. Belg* 28, 308-309 (1914/15). (2) Pinner, *Ann.* 179, 75. (3) Oddo, Marneli, *Gazz. chim. ital.* 33, II 412-414 (1903). (4) Neher, Fleece, *em. Soc.* 48, 2422-2423 (1926). (5) Magnani, McElvain, *J. Am. Chem. Soc.* 60, 2210-3 (6) Lieben, *Ann.* 104, 114-115 (1857) (7) I G, French 814,435, June 23, 1937; 11 3066, C A 32, 1390 (1938). (8) Ger. 528,194, June 26, 1931; *Cent.* 1931, II 1910. 1, *Ann.* 279, 300 (1894). (10) Böescken, Tellegen, Plusje, *Rec. trav. chim.* 57, 75 (1938). attaway, Backeberg, *J. Chem. Soc.* 125, 1101 (1924). (12) Jacobsen, *Ber.* 4, 217 (1871). r, Foster, *J. Am. Chem. Soc.* 31, 414 (1909). (14) Paterno, *Ann.* 149, 373 (1869). r, *Jahresber.* 1876, 475 (16) Wohl, Roth, *Ber.* 40, 217 (1907). (17) Pinner, *Ber.* 5, 1872).

***d,l*- $\alpha$ -CHLOROPROPIONIC ACID**  $C_3H_5O_2Cl$  Beil. II - 248  
(2-Chloropropanoic acid)  $CH_3-CH.COOH$  II-(110)  
Cl II-(226)

$86^\circ$  cor. (1)  $D_4^{20} = 1.2585$  (6)  $n_D^{20} = 1.4350$  (6)

$86^\circ$  (2)

$85.2^\circ$  at 760 mm. (3)  $n_D^{19.4} = 1.4364$  (3)

$85^\circ$  (4)

$88.0-89.4^\circ$  at 15 mm. (3)

$83.5-84.5^\circ$  at 12 mm. (5)

less liq. with weak odor suggestive both of acetic acid and butyric acid; misc. with ether; volatile with steam, blisters skin.

prepn. of  $\bar{C}$  from propionic acid (1:1025) with  $Cl_2$  (7) (8) or with  $SO_2Cl_2$  + dibenzoyl e in  $CCl_4$  (9) see indic. refs.; from  $\alpha$ -chloropropionyl chloride (3:5320) by hydrolysis (11) (12) with water see indic. refs.; from  $\alpha$ -chloropropionitrile by hydrolysis with HCl see (5); from 2-chloropropanol-1 (3:7917) (4) or from 3-chlorobutanone-2 ( $\alpha$ -thyl methyl ketone) (3:7598) (13) (14) by oxidn. with  $HNO_3$  or other oxidn. agts. ic. refs.]

n treatment with  $Cl_2$  as specified (15) yields  $\alpha,\beta$ -dichloropropionic acid (3:0855);  $SOCl_2$  yields (16)  $\alpha$ -chloropropionyl chloride (3:5320), b.p.  $111^\circ$ ;  $\bar{C}$  on reduction n + HCl yields (10) propionic acid (1:1025) [for study of catalytic hydrogenation r its salts see (17)];  $\bar{C}$  with  $SO_3$  at  $170^\circ$  yields (18)  $\alpha$ -chloro- $\alpha$ -sulfopropionic acid actn. of  $\bar{C}$  with sulfites see (2)],  $\bar{C}$  with conc. aq.  $NH_4OH$  gives (43-46% yield (19)) nine ( $\alpha$ -aminopropionic acid) [for behavior of  $\bar{C}$  with liq.  $NH_3$  see (20) (21)].]

n alk. hydrolysis gives (10) (22) lactic acid (1:0400) [for study of rate of hydrolysis 23) or its sodium salt (24) see indic. refs.].

on htg. with pyridine at  $100^\circ$  loses  $CO_2$  and yields (25) ethylpyridinium chloride.]

n conversion to salt, treatment with KCN, and subsequent acidification yields (26) ymalonic acid, m.p.  $132^\circ$  (has been used for ident. of  $\bar{C}$  (26)).



[ $\bar{C}$  with  $Cl_2$  in pres. of Fe gives (16) dichloromaleyl (di)chloride (3:6197) q.v. —  $\bar{C}$  with  $Br_2$  in dark does not react, but in direct sunlight for 5 hrs. adds 82% of theoretical amt. yielding (2)  $\alpha$ -chloro- $\alpha,\beta$ -dibromosuccinyl (di)chloride, b.p. 116–118° at 10 mm. (2), which on hydrolysis with aq. gives (2)  $\alpha$ -chloro- $\alpha,\beta$ -dibromosuccinic acid, hydrated pr. from HCl, m.p. 65–75°, which after drying over conc.  $H_2SO_4$  gives anhydrous form, m.p. 139–140° (2).]

[ $\bar{C}$  with 3 N EtOH/KOH (large excess) in freezing mixt. loses HCl and hydrolyzes (or vice versa) and after acidification as directed gives K H acetylenedicarboxylate which with aq. at 100° for 1 hr. loses  $CO_2$  giving (39% yield from  $\bar{C}$  (12)) propiolic acid [Beil. II-477,  $\Pi_1$ -(208),  $\Pi_2$ -(449).]

[ $\bar{C}$  with MeOH under reflux yields (13) dimethyl chlorofumarate (3:6582);  $\bar{C}$  with EtOH yields (1) (9) (15) diethyl chlorofumarate (3:6564); note that  $\bar{C}$  reacts with MeOH or with aniline much more rapidly than the isomeric chloromaleyl (di)chloride (3:6158) (for details and graphs see (2)).]

$\bar{C}$  (1 mole) with chlorofumaric acid (3:4853) (1 mole) at 125° for 1 hr. gives (11) chloromaleic anhydride (3:0280), m.p. 33°.

[ $\bar{C}$  with  $AlCl_3$  combines yielding a viscous oil, solidifying in freezing mixt. to yel. cryst., m.p. about 50°; this prod. with water regenerates  $\bar{C}$  but if first htd. at 100° for several hrs. and then treated with aq. gives (S5–S7% yield (2)) (3) chloromaleyl (di)chloride (3:6158).]

$\bar{C}$  with excess conc. aq.  $NH_4OH$  reacts vigorously yielding (1) (11) chlorofumaric acid diamide, ndls. from alc., m.p. 187° (11).

[ $\bar{C}$  in aq. AcOH (1:4) with hydrazine hydrate as directed gives hydrazine salt of  $N,N$ -bis ( $\alpha$ -chloro- $\beta$ -carboxyacryloyl)hydrazine (2), m.p. 215° (9); note that  $\bar{C}$  with  $NH_2.NH_2.H_2O$  in ether, pet. eth., or AcOH gives only (9) resinous or amorphous yel. prods.]

$\bar{C}$  (1 mole) with  $p$ -chloroaniline (4 moles) in dry ether reacts vigorously giving mainly (11) chlorofumaro-di- $p$ -chloroanilide, pale yel. ndls. from alc., m.p. 223° (11), accompanied by a little  $N$ -( $p$ -chlorophenyl)chloromaleimide, pl. from alc. mother liquor, m.p. 175° (11).

$\bar{C}$  on hydrolysis with aq. yields chlorofumaric acid (3:4853), m.p. 193°.

3:6105 (1) Perkin, *J. Chem. Soc.* 53, 695–697, 700 (1888). (2) Ott, *Ann.* 392, 258–259, 263–264, 278–285 (1912). (3) Dann, Davies, Hambly, Paul, Semmens, *J. Chem. Soc.* 1933, 15–21. (4) von Auwers, Schmidt, *Ber.* 46, 481 (1913). (5) Ruggli, *Helv. Chim. Acta* 3, 569 (1920). (6) Diels, Thiele, *Ber.* 71, 1174–1175 (1938). (7) Gladstone, *J. Chem. Soc.* 59, 293 (1891). (8) von Auwers, Harres, *Ber.* 62, 1679 (1929). (9) Ruggli, Hartmann, *Helv. Chim. Acta* 3, 512–514 (1920). (10) Perkin, Duppa, *Ann.* 115, 105–107 (1860).

(11) Chattaway, Parkes, *J. Chem. Soc.* 125, 466–468 (1924). (12) Ingold, *J. Chem. Soc.* 127, 1202–1203 (1925). (13) Kauder, *J. prakt. Chem.* (2) 31, 24–38 (1885). (14) Zetsche, Hubacher, *Helv. Chim. Acta* 9, 292–293 (1926). (15) Claus, *Ann.* 191, 80–93 (1878). (16) Vandervelde, *Bull. acad. roy. Belg.* (3) 37, 680–700 (1899); *Cent.* 1900, 1 404.

### 3:6110 DICHLOROACETALDEHYDE



Beil. I - 614

DIETHYLACETAL



$I_1$ -(328)

("Dichloroacetal")

$I_2$ -(677)

B.P. 185–186°

(1)

$D_4^{14} = 1.1383$  (6)

183–184°

(2)

182–184°

(3)

181–184°

(4)

178–181° at 760 mm. (5)

66–71° at 12 mm. (5)

$\bar{C}$  undergoes sl. decompn. on stdg. or distn. — [For use as insecticide see (7) (8).]

[For prepn. of  $\bar{C}$  from acetaldehyde diethylacetal (1:0156) by actn. of  $Cl_2$  (37% yield (5)) see (5) (17); from ethyl alcohol (1:6130) by actn. of  $Cl_2$  (yield 75% (1), 40% (10),

0% (5); see (1) (10) (5) (6) (11); from  $\alpha,\beta,\beta$ -trichlorodiethyl ether + Zn (78% yield (4)), or abs. alc. (3), or NaOEt (12), or even water (3); from  $\alpha,\beta,\beta,\beta$ -tetrachlorodiethyl ether with Zn + abs. alc. (13).]

$\bar{C}$  on warming with conc.  $H_2SO_4$  (14) (2) or on htg. at  $150^\circ$  with conc. HCl (15) or on htg. with benzoic anhydride + a little conc.  $H_2SO_4$  gives (yield 81% (1), 78% (10), 71% (16)) dichloroacetaldehyde (3:5180), b.p.  $90-91^\circ$ .

$\bar{C}$  on htg. with alc. NaOH at  $160-180^\circ$  yields (17) glyoxal tetraethylacetal [Beil. I-760], h.p.  $180^\circ$  (17). —  $\bar{C}$  with K *ter*-butylate loses HCl yielding (5) chloroketene diethylacetal, h.p.  $166^\circ$  at 732-740 mm.,  $D_{15}^{15} = 1.0534$ ,  $n_D^{25} = 1.4375$  (5).

$\bar{C}$  with  $PCl_5$  yields (15)  $\alpha,\beta,\beta$ -trichlorodiethyl ether [Beil. I-615].

3:6110 (1) van de Walle, *Bull. soc. chim. Belg.* 23, 308-309 (1914/18). (2) Pinner, *Ann.* 179, 33-34 (1875). (3) Oddo, Mameli, *Gazz. chim. ital.* 33, II 412-414 (1903). (4) Neher, Fleece, *J. Am. Chem. Soc.* 48, 2422-2423 (1926). (5) Magnani, McElvain, *J. Am. Chem. Soc.* 60, 2210-2213 (1938). (6) Lieben, *Ann.* 104, 114-115 (1857). (7) I.G., French 814,435, June 23, 1937; *Cent.* 1937, II 3066, *C.A.* 32, 1390 (1938). (8) Ger 528,194, June 26, 1931; *Cent.* 1931, II 1910. (9) Fritsch, *Ann.* 279, 300 (1894).

(11) Chattaway, Backeberg, *J.*

(13) Neher, Foster, *J. Am. Chem.*

(15) Krey, *Jahresber.* 1876, 475.

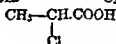
148-151 (1872).

### 3:6125 *d,l*- $\alpha$ -CHLOROPROPIONIC ACID

(2-Chloropropanoic acid)

$C_3H_5O_2Cl$

Beil. II - 248



$\Pi_1$ -(110)

$\Pi_2$ -(226)

B.P.  $186^\circ$  cor.

(1)

$D_4^{20} = 1.2585$  (6)

$n_D^{20} = 1.4350$  (6)

$186^\circ$

(2)

$185.2^\circ$  at 760 mm. (3)

$n_D^{19.4} = 1.4364$  (3)

$185^\circ$

(4)

$88.6-89.4^\circ$  at 16 mm. (3)

$83.5-84.5^\circ$  at 12 mm. (5)

Colorless liq. with weak odor suggestive both of acetic acid and butyric acid; misc. with aq. alc. or ether; volatile with steam; blisters skin.

[For prepn. of  $\bar{C}$  from propionic acid (1:1025) with  $Cl_2$  (7) (8) or with  $SO_2Cl_2$  + dibenzoyl peroxide in  $CCl_4$  (9) see indic. refs., from  $\alpha$ -chloropropionyl chloride (3:5320) by hydrolysis (1) (10) (11) (12) with water see indic. refs.; from  $\alpha$ -chloropropionitrile by hydrolysis with conc. HCl see (5); from 2-chloropropanol-1 (3:7917) (4) or from 3-chlorobutanone-2 ( $\alpha$ -chloroethyl methyl ketone) (3:7598) (13) (14) by oxida. with  $HNO_3$  or other oxida. agts. see indic. refs.]

[ $\bar{C}$  on treatment with  $Cl_2$  as specified (15) yields  $\alpha,\beta$ -dichloropropionic acid (3:0855);  $\bar{C}$  with  $SOCl_2$  yields (16)  $\alpha$ -chloropropionyl chloride (3:5320), h.p.  $111^\circ$ ;  $\bar{C}$  on reduction with Zn + HCl yields (10) propionic acid (1:1025) [for study of catalytic hydrogenation of  $\bar{C}$  or its salts see (17)];  $\bar{C}$  with  $SO_2$  at  $170^\circ$  yields (18)  $\alpha$ -chloro- $\alpha$ -sulfopropionic acid [for reactn. of  $\bar{C}$  with sulfites see (2)];  $\bar{C}$  with conc. aq.  $NH_4OH$  gives (43-46% yield (19)) *d,l*-alanine ( $\alpha$ -aminopropionic acid) [for behavior of  $\bar{C}$  with liq.  $NH_3$  see (20) (21)].

$\bar{C}$  on alk. hydrolysis gives (10) (22) lactic acid (1:0400) [for study of rate of hydrolysis of  $\bar{C}$  (23) or its sodium salt (24) see indic. refs.].

$\bar{C}$  on htg. with pyridine at  $100^\circ$  loses  $CO_2$  and yields (25) ethylpyridinium chloride.]

$\bar{C}$  on conversion to salt, treatment with KCN, and subsequent acidification yields (26) methylmalonic acid, m.p.  $132^\circ$  (has been used for ident. of  $\bar{C}$  (26)).

$\bar{C}$  with *o*-phenylenediamine in 5 *N* HCl refluxed 3 hrs. gives (yields: 61-64% (35), 55-60% (36)) 2 ( $\alpha$ -chloroethyl)benzimidazole, ndls. from hot  $C_6H_6$ , m.p. 134.7-135.4° cor. (35) 134-135° cor. (36).

— Methyl  $\alpha$ -chloropropionate: b.p. 132°. (See 3:7908.)

— Ethyl  $\alpha$ -chloropropionate: b.p. 147°. (See 3:8125.)

①  $\alpha$ -Chloropropionamide: m.p. 80° (27). [From ethyl  $\alpha$ -chloropropionate (3:8125) with conc. aq.  $NH_4OH$  (27).]

②  $\alpha$ -Chloropropion-anilide: lfts. from lgr., m.p. 92° (28) (9). [From  $\alpha$ -chloropropionyl chloride (3:5320) + aniline in  $CHCl_3$  (28).] [Note that the reactn. prod. of this compd. with more aniline, viz.,  $\alpha$ -anilinopropionanilide [Beil. XII-558], has m.p. 126°.]

③  $\alpha$ -Chloropropion-*p*-toluidide: lfts. from lgr., m.p. 124° (28), 108° (29). [From  $\alpha$ -chloropropionyl chloride (3:5320) with 2 moles *p*-toluidine (28).] [Note that the reactn. prod. of this compd. with more *p*-toluidine, viz.,  $\alpha$ -(*p*-toluidino)propion-*p*-toluidide [Beil. XII-980] has m.p. 158°.]

④ Phenylhydrazine  $\alpha$ -chloropropionate: m.p. 95° (30). [From  $\bar{C}$  + phenylhydrazine (30).]

⑤  $\alpha$ -Phenoxypropionic acid: ndls. from aq., m.p. 115-116° (31), 115° (32). [From sodium  $\alpha$ -chloropropionate + sodium phenolate on htg. and evapn. (33).] [Note that the opt. act. forms of this deriv. melt at 87° (32).]

3:6125 (1) Buchanan, *Ann.* 148, 170 (1868). (2) Backer, von Mels, *Rec. trav. chim.* 49, 177-191, 363-380 (1930). (3) Burkard, Kahovec, *Monatsh.* 71, 340 (1938). (4) Henry, *Bull. acad. roy. Belg.* 1903, 397-431; *Cent.* 1903, II 486. (5) Michael, *Ber.* 34, 4040-4050 (1901). (6) Schjanberg, *Z. physik. Chem.* A-172, 230 (1933). (7) Bass, Burlew (to Dow Chem. Co.), U.S. 1,993,713, March 5, 1935; *Cent.* 1935, II 1257; *C.A.* 29, 2350 (1935). (8) Bass (to Dow Chem. Co.), U.S. 2,010,685, Aug. 6, 1935; *Cent.* 1935, I 880; *C.A.* 29, 6608 (1935). (9) Kharasch, Brown, *J. Am. Chem. Soc.* 62, 925-929 (1940). (10) Ulrich, *Ann.* 109, 269-271 (1859).

(12) Lovén, *J. prakt. Chem.* (2) 29, 367 (1884). U.S. 2,031,470, Aug. 18, 1936; *Cent.* 1936, II

Ascho Petrol.

*Cent.* 1936, II

133, II 1587.

331). (18) I

*J. Soc.* 39, 830 (1937). (20) Cheronis, Spitz-

78 (1941). (22) Wichelhaus, *Ann.* 143, 4-5

(1935). (24) Simpson, *J. Am. Chem. Soc.* 40,

*prakt. Chem.* (2) 96, 53-54 (1917). (26) Bloom-

(27) Deckarts, Otto, *Ber.* 9, 1592 (1876). (28)

(30)

(1867). (23) Kailan, Kunze, *Monatsh.* 71, 678 (1918). (25) von Walther, Weinhausen, field, Farmer, *J. Chem. Soc.* 1932, 2076-2077. Bischoff, Walden, *Ann.* 277, 277-278 (1894). Stempel, Schaffel, *J. Am.*

(31) Bischoff, *Ber.* 33,

992 (1922). (33) Saarha

*rec. chim. Belg.* 45, 255 (1907). (34) Swager, *Ber.* 34, 1111 (1901). (35) Aschoff,

Miller, Day, *J. Am. Chem. Soc.* 65, 1856 (1943).

(4) 31,

*Bull.*

(30)

3:6135

$n$ -PROPYL TRICHLOROACETATE

$n$ -C<sub>3</sub>H<sub>7</sub>O.CO.CCl<sub>3</sub>

$C_6H_7O_2Cl_3$

Beil. II - 209

$\Pi_1$ —

$\Pi_2$ —

B.P.					
186.9-187.1°	(1)	$D_4^{20} = 1.3221$	(6)	$n_D^{20} = 1.4501$	(6)
186.5-187° at 763 mm.	(2)	1.3213	(5)	1.4507	(5)
187°	(3)	$D_4^{15} = 1.3170$	(4)	$n_D^{15} = 1.4508$	(4)
117-117.3° at 130 mm.	(1)				
69° at 10 mm.	(4)				
65.0-65.5° at 5 mm.	(5)				

[For prepn. (57% yield (4)) from *n*-propyl alc. (1:6150) + trichloroacetic ac. (3:1150) see (4).]

[For study of chlorination of  $\bar{C}$  see (4).]

For study of hydrolysis of  $\bar{C}$  see (5).

3:6135 (1) Cheng, *Z. physik. Chem. B-24*, 307 (1934). (2) Schiff, *Z. physik. Chem.* 1, 379 (1887). (3) Clermont, *Bull. soc. chim.* (2) 40, 302 (1883). (4) Gayler, Waddie, *J. Am. Chem. Soc.* 63, 3358-3359 (1942). (5) Palomaa, Salma, Korte, *Ber.* 72, 797 (1939). (6) Schjanberg, *Z. physik. Chem. A-172*, 229 (1935).

3:6140

ISOBUTYL TRICHLOROACETATE

$(CH_3)_2CH\ CH_2\ O.CO\ CCl_3$

$C_6H_9O_2Cl_3$

Beil. II - 209

$\Pi_1$ —

$\Pi_2$ —

B.P. 187-189°	(1)	$D_4^{25} = 1.255$	(2)	$n_D^{25} = 1.4456$	(2)
93-94° at 24 mm.	(2)	$D_4^{20} = 1.2636$	(3)	$n_D^{20} = 1.4483$	(3)

Colorless liq. of agreeable odor (1).

[For prepn. (82-89% yield (2)) from isobutyl alc. (1:6165) + trichloroacetic ac. (3:1150) see (2) (1).]

[For study of chlorination of  $\bar{C}$  see (2).]

3:6140 (1) Judson, *Ber.* 3, 784 (1870). (2) Waddie, Adkins, *J. Am. Chem. Soc.* 61, 3361-3364 (1939). (3) Schjanberg, *Z. physik. Chem. A-172*, 229 (1935)

3:6150

1,2,3,4-TETRACHLOROBUTADIENE-1,3

(Liquid stereoisomer)

$C_4H_2Cl_4$

Beil. S.N. 12

$HC=C-C=CH$

$\begin{array}{cccc} | & | & | & | \\ Cl & Cl & Cl & Cl \end{array}$

B.P. 188°	(1)	$D_{15}^{15} = 1.516$	(1)
67-68° at 10 mm.	(1)		
43° at 1 mm.	(1)		

[See also the solid stereoisomer (3:6570), *m.p.* 50°.]

Colorless strongly refractive liq. with agreeable honey-like odor; on stdg. turns brown and evolves HCl.

[For isolation of  $\bar{C}$  from the high-boil. fractn. resulting in the preparation of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1); for prepn. of  $\bar{C}$  from 1,1,2,3,4,4-hexachlorobutane (3:3155) with alc. KOH at room temp. see (1).]

2 (3:9046), b.p. 97° at 10 mm. (1). [Note that  $\bar{C}$  does not (1) yield octachlorobutane (3:2000).]

$\bar{C}$  with  $Br_2$  yields 1,4-dibromo-1,2,3,4-tetrachlorobutene-2, long colorless doubly refracting ndls., m.p. 105° (1).

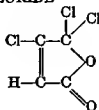
$\bar{C}$  does not react with conc.  $HNO_3$ , but with fuming  $HNO_3$  or even with  $NO_2$  gas  $\bar{C}$  reacts vigorously pptg. 1,4-dinitro-1,2,3,4-tetrachlorobutene-2, colorless cryst. from  $AcOH$ , m.p. 131° (1). [Note that this prod. cannot be recryst. from alc. since it reacts yielding ethyl nitrite and a yel. viscous oil (1).]

3:6150 (1) Müller, Huther, *Ber.* 64, 589-600 (1931); *C.A.* 25, 3956 (1931).

### 3:6158 CHLOROMALEYL (DI)CHLORIDE

 $C_4HO_2Cl_2$ 

Beil. XVII—

XVII<sub>1</sub>-(138)

B.P.		M.P.			
189.3°	at 760 mm. (1)	12.7° (1)	$D_4^{20} = 1.602$ (3)	$n_D^{20} = 1.5126$ (3)	
186.3°	at 760 mm. (1)	11-12° (2)			
185.2°	at 730 mm. (1)		$D_4^{18.1} = 1.6049$ (3)	$n_D^{18.1} = 1.51362$ (3)	
104.0-105°	at 50 mm. (2)				
82.2-82.5°	at 26 mm. (3)		$D_4^{17.5} = 1.6044$ (3)	$n_D^{17.5} = 1.51375$ (3)	
71.5°	at 10 mm. (1)				

[See also chlorofumaryl (di)chloride (3:6105).]

$\bar{C}$  is generally formulated in the unsymmetrical structure shown above (for discussion see (1) (2)); note, however, that the position of the chlorine atom attached to the carbon bearing the double bond is frankly assumed and may be on the other such carbon.

Note also that  $\bar{C}$  appears to exist also in a labile form, m.p. 4.8° (1), which readily changes to the higher-melting (stable) variety;  $\bar{C}$  on supercooling and inoculation with the labile form cryst. in the latter.

$\bar{C}$  from pet. ether cryst. as needles;  $\bar{C}$  has disagreeable odor (1) and is far more lachrymatory than the isomeric chlorofumaryl (di)chloride (3:6105) (2).

[For prepn. of  $\bar{C}$  from chlorofumaryl (di)chloride (3:6105) by combination with  $AlCl_3$ , htg. at 100° for several hrs., and subsequently decomposing with ice water (yield as high as 85-87% but varies according to nature of  $AlCl_3$  used) see (1) (2).]

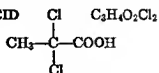
[ $\bar{C}$  on hydrogenation in dry ether in pres. of Pt black yields (4) *n*-butyric acid (1:1035) and other prods.]

[ $\bar{C}$  with  $AlCl_3$  gives a cpd., red-brown ndls., m.p. abt. 100° (1); on htg. at 180-225° this prod. decomposes yielding (1)  $\alpha,\beta$ -dichloroacryloyl chloride (see under 3:2265), b.p. 147.3° at 733 mm., phosgene (3:5000),  $CO$ ,  $HCl$ , and other prods.]

$\bar{C}$  on protracted boilg. is converted (1) to chlorofumaryl (di)chloride (3:6105).

[ $\bar{C}$  reacts with  $MeOH$  and with aniline much more slowly than the isomeric chlorofumaryl (di)chloride (3:6105) (for details and graphs see (1) cf. (2)).]

3:6158 (1) Ott, *Ann.* 392, 255-265, 278-285 (1912). (2) Dann, Davies, Hambly, Paul, *Semmens, J. Chem. Soc.* 1933, 15-21. (3) von Auwers, Schmidt, *Ber.* 46, 482 (1913). (4) Ott, *Ber.* 46, 2173-2175 (1913).

3:6162  $\alpha,\alpha$ -DICHLOROPROPIONIC ACID $\text{C}_3\text{H}_4\text{O}_2\text{Cl}_2$ 

Beil. II - 250

II<sub>1</sub>—II<sub>2</sub>-(228)

B.P. [185-190°] (1) (4) (6)

186-189° (7)

00-92° at 14 mm. (2)

 $D_4^{22.8} = 1.389$  (2)

Colorless liq. — Very eas. sol. aq. or alc.; from aq. solns. can be salted out with NaCl. — Volatile with steam without hydrolysis — Insol. conc. HCl.

[For prepn. of  $\bar{\text{C}}$  from corresp. acid chloride, viz.,  $\alpha,\alpha$ -dichloropropionyl chloride (3:5372), by hydrolysis see (3); from  $\alpha,\alpha$ -dichloropropionitrile monomer [Beil. II-251] (1) (4) (19),  $\alpha,\alpha$ -dichloropropionitrile dimer [Beil. II-252] (5), or  $\alpha,\alpha$ -dichloropropionitrile trimer [Beil. XXVI-38] (6) (7) by hydrolysis with  $\text{H}_2\text{SO}_4$  see indic. refs.; from  $\alpha,\alpha$ -dichloropropionanilide (see below) by hydrolysis with conc. HCl in s.t. at 140° see (2); for formn. of  $\bar{\text{C}}$  from propionic acid with  $\text{Cl}_2$  under certain conditions see (26).]

$\bar{\text{C}}$  is reduced by Zn + dil.  $\text{H}_2\text{SO}_4$  giving (1) propionic acid (1:1025).

$\bar{\text{C}}$  on keeping gradually splits off some HCl (2). —  $\bar{\text{C}}$  with alc. KOH on boilg. either loses HCl giving (8)  $\alpha$ -chloroacrylic acid (3:1445) or by some obscure mechanism gives (9) cf. (10) (11)  $\beta$ -ethoxyacrylic acid [Beil. III-369], m.p. 110°.

$\bar{\text{C}}$  as a monobasic acid forms corresp. salts; e.g.,  $\text{NH}_4\bar{\text{A}}$  (1),  $\text{K}\bar{\text{A}} \cdot 6\text{H}_2\text{O}$  (1);  $\text{Ca}\bar{\text{A}}_2 \cdot 3\text{H}_2\text{O}$  (1);  $\text{Ba}\bar{\text{A}}_2 \cdot \text{H}_2\text{O}$  (1);  $\text{Zn}\bar{\text{A}}_2 \cdot \text{H}_2\text{O}$  (1) (12),  $\text{Ag}\bar{\text{A}}$ , spar. sol. aq. (1), note that this dry  $\text{Ag}\bar{\text{A}}$  at 60° decomposes violently giving (12) AgCl and a mixed anhydride of  $\bar{\text{C}}$  with pyruvic acid, viz.,  $\text{CH}_3\text{C}(\text{Cl}_2)\text{CO O.CO.CO.CH}_3$ ; however,  $\text{Ag}\bar{\text{A}}$  on warming with aq. gives (12) AgCl + pyruvic acid (1:1040) and/or (1)  $\alpha$ -chloroacrylic acid (3:1445).

$\bar{\text{C}}$  with aq.  $\text{Ag}_2\text{O}$  or  $\text{Ag}_2\text{CO}_3$  on protracted hgt. gives (13) (12) pyruvic acid (1:1040), but use of excess  $\text{Ag}_2\text{O}$  (14) (1) cf. (15) leads to  $\text{AcOH}$  (1:1010) +  $\text{CO}_2$  +  $\text{H}_2\text{O}$ . —  $\bar{\text{C}}$  with aq.  $\text{Ba}(\text{OH})_2$  on boilg. or  $\bar{\text{C}}$  with aq. in s.t. at 120-150° gives (14) (16) pyruvic acid (1:1040).

[ $\bar{\text{C}}$  with finely divided Ag in  $\text{C}_6\text{H}_6$  on refluxing 40-70 hrs. gives (17) (18) (19)  $\alpha,\alpha'$ -dimethylmaleic anhydride [Beil. XVII-445], m.p. 95°, and  $\alpha,\alpha'$ -dichloro- $\alpha,\alpha'$ -dimethylsuccinic acid [Beil. II-668], m.p. 185°.]

[ $\bar{\text{C}}$  (3 moles) with  $\text{PCl}_3$  (1 mole) gives (3) (20)  $\alpha,\alpha$ -dichloropropionic acid anhydride [Beil. II-251], b.p. 196-200° (20), 190-192° (3). —  $\bar{\text{C}}$  (3 moles) with  $\text{PCl}_3$  (2 moles) (3) or with  $\text{SOCl}_2$  refluxed for 10 hrs. (21) gives  $\alpha,\alpha$ -dichloropropionyl chloride (3:5372).]

$\bar{\text{C}}$  with alcohols in pres. of dry HCl gives (1) the corresp. esters (see also below).

— Methyl  $\alpha,\alpha$ -dichloropropionate: b.p. 144-146° (7), 143-144 u.c. (1). [From  $\bar{\text{C}}$  with  $\text{MeOH}$  + dry HCl (1) (7); for study of kinetics of hydrolysis see (22).]

— Ethyl  $\alpha,\alpha$ -dichloropropionate: b.p. 160° (23), 156-157° (1) (6), 83-85° at 53 mm. (2). [From  $\bar{\text{C}}$  with  $\text{EtOH}$  + dry HCl (1) or from  $\alpha,\alpha$ -dichloropropionyl chloride (3:5372) with  $\text{EtOH}$  (23); note that this ester with aq. in s.t. at 130° gives (16) (14) undergoes hydrolysis yielding pyruvic acid (1:1010) and ethyl pyruvate (1:3308) or with aq.  $\text{Ag}_2\text{O}$  gives (15) Ag acetate.]

①  $\alpha,\alpha$ -Dichloropropionamide: lfts. from dil. alc., m.p. 117-118° (2) (24), 117° (12), 116-117° (3), 116° (23) (5) (20), 115-116° (4) (6) (7). [From ethyl  $\alpha,\alpha$ -dichloropropionate (above) (3) (23), from methyl  $\alpha,\alpha$ -dichloropropionate (above) (7), or from  $\alpha,\alpha$ -dichloropropionyl chloride (3:5372) (3) with conc. aq.  $\text{NH}_4\text{OH}$ .]

②  $\alpha,\alpha$ -Dichloropropion-*N*-ethylamide: m.p. 51-52° (2). [From  $\bar{\text{C}}$  with  $\text{EtNH}_2$ .]

—  $\alpha,\alpha$ -Dichloropropionanilide: m.p. 101° (2). [Reported only by indirect means (2).]

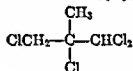
—  $\alpha,\alpha$ -Dichloropropion-*p*-toluidide: m.p. 81-86° (25). [Reported only by indirect means (25).]

3:6162 (1) Beckurts, Otto, *Ber.* 9, 1876-1881 (1876). (2) von Braun, Jostes, *Münch. Ann.* 453, 134-135 (1927). (3) Beckurts, Otto, *Ber.* 11, 386-391 (1878). (4) Beckurts, Otto, *Ber.* 9, 1593-1594 (1870). (5) Tröger, J. *prakt. Chem.* (2) 46, 302-363 (1892). (6) Beckurts, Otto, *Ber.* 10, 263-264 (1877). (7) Otto, Voigt, J. *prakt. Chem.* (2) 36, 84-85 (1887). (8) Otto, Beckurts, *Ber.* 18, 241-242 (1885). (9) Otto, *Ber.* 23, 1198-1110 (1890). (10) Claisen, *Ber.* 31, 1020 (1898).

(11) Tschitschibabin, J. *prakt. Chem.* (2) 73, 335 (1900). (12) Beckurts, Otto, *Ber.* 18, 228-235 (1885). (13) Beckurts, Otto, *Ber.* 19, 265-266 (1877). (14) Beckurts, Otto, *Ber.* 19, 2037-2039 (1877). (15) Klimenko, *Ber.* 7, 1405-1406 (1874). (16) Klimenko, *Ber.* 5, 477 (1872). (17) Beckurts, Otto, *Ber.* 19, 1503-1504 (1877). (18) Otto, Beckurts, *Ber.* 18, 826-830, 836, 847 (1885). (19) Otto, Holst, J. *prakt. Chem.* (2) 41, 461-467 (1890). (20) Otto, Holst, J. *prakt. Chem.* (2) 42, 78 (1890).

(21) Leimu, *Ber.* 70, 1050 (1937). (22) Burki, *Helv. Chim. Acta* 1, 244-245 (1918). (23) Klimenko, *Ber.* 3, 466-467 (1870). (24) Otto, *Ann.* 132, 183 (1864). (25) Bischoff, Walden, *Ann.* 279, 93 (1894). (26) Röhms and Haas, A.G., *Ger.* 579,054, June 29, 1933; *Cent.* 1933 II 1587; [*C.A.* 28, 1050 (1934)].

3:6165 1,1,2,3-TETRACHLORO-2-METHYLPROPANE  $C_4H_2Cl_4$  *Bell. S.N.* 10



B.P.

M.P.

100.6-101.3° cor. (1)

-40° (1)

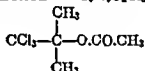
 $D_4^{25} = 1.4303$  (1) $n_D^{20} = 1.4063$  (1)

[For formn. of  $\bar{C}$  (together with other products) from *ter*-butyl chloride (3:7045) or from 1,3-dichloro-2-methylpropane (3:7960) +  $Cl_2$  see (1).]

3:9165 (1) Rogers, Nelson, *J. Am. Chem. Soc.* 58, 1027-1029 (1936).

3:0180  $\beta, \beta, \beta$ -TRICHLORO-*ter*-BUTYL ACETATE  $C_6H_9O_2Cl_3$   
("Acetone-chloroform" acetate;  
"chloretoone" acetate)

*Bell. II* - 131  
 $H_1$  - (50)  
 $H_2$  -



B.P. 191°

(1)

190-191°

(2)

151-152° at 237 mm. (3)

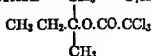
Colorless mobile liq. with agreeable odor (1). Insol. nq.; eas. sol. alc., ether, acetone,  $CHCl_3$ ,  $C_6H_6$  (3). — Volatile with steam (3).

$\bar{C}$  on boilg. with 3-4 vols. conc.  $HNO_3$  is rapidly hydrolyzed; after boilg. only a few min. addn. of nq. ppts.  $\beta, \beta, \beta$ -trichloro-*ter*-butyl alc. (3:2662), m.p. 78° (3). [ $\bar{C}$  hydrolyzes only very slowly (108 hrs.) on boilg. with aq. alone; in pres. of dil.  $H_2SO_4$  hydrolysis is more rapid (7 hrs.) and  $\beta, \beta, \beta$ -trichloro-*ter*-butyl alc. (chloretoone) sublimes into condenser (3).]

[For prepn. from  $\beta, \beta, \beta$ -trichloro-*ter*-butyl alc. (3:2662) +  $Ac_2O$  (1) or  $Ac_2O$  +  $NaOAc$  (3) see (1) (3).]

3:6180 (1) Willgerodt, Dürr, J. *prakt. Chem.* (2) 39, 285 (1889). (2) Taffe, *Roczniki Farm.* 2, 99-107 (1923); *Cent.* 1924, II 304. (3) Aldrich, *J. Am. Chem. Soc.* 37, 2720-2723 (1915).

3:6185 *ter*-AMYL TRICHLOROACETATE  $\text{CH}_3$   $\text{C}_7\text{H}_{11}\text{O}_2\text{Cl}_3$  Beil. S.N. 160



B.P. 191° at 756 mm. (1)  
105° at 30 mm. (1)

$D_{20}^{20} = 1.2505$  (1)

$\bar{C}$  on distn. tends to decompose into 2-methylbutene-2 (1:8220) + trichloroacetic acid (3:1150) (1).

[For studies on prepn. from 2-methylbutene-2 (1:8220) + trichloroacetic acid (3:1150) see (2) (3) (4) (5) (6); for prepn. (84% yield (1)) from *ter*-amyl alc. (1:6160) and trichloroacetic ac. (3:1150) see (1).]

3:6185 (1) Liston, Dehn, *J. Am. Chem. Soc.* 60, 1264-1265 (1938). (2) Timofeev, Andreasov, *J. chim. Ukraine* 1, 107-110 (1925); *C.A.* 20, 2820 (1926). (3) Timofeev, Israilevich, Chaskes, *em. Zhur. Ukrain. ndreasov*.

— TRICHLOROMETHYL TRICHLOROACETATE  $\text{Cl}_3\text{C.COOCCL}_3$  Beil. III - 17  
III<sub>1</sub>—  
III<sub>2</sub>—

B.P. 101-102°

M.P. 34°

$D_4^{35} = 1.67331$

See 3:0290. Division A: Solids.

3:6105 *m*-CHLOROANISOLE  
(*m*-Chlorophenyl  
methyl ether)



$\text{C}_7\text{H}_7\text{OCl}$

Beil. VI - 185  
VI<sub>1</sub>-(100)

B.P.

193-194° (1)

$D_4^{12.0} = 1.1759$  (4)  $n_{D_4}^{12.0} = 1.53783$  (4)

193° (2)

191-192° at 728 mm. (3)

Od. — Volatile with steam (3). — Odor like nnisole (5). — Sol. alc., ether.

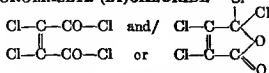
[For prepn. of  $\bar{C}$  from *m*-chlorophenol (3:0255) by htg. with KOH + MeI in MeOH (1) or  $\text{Me}_2\text{SO}_4$  + alk. (7) see (1) (7); from *m*-chloroaniline by diazotization and warming with MeOH see (2); from *m*-aminophenyl methyl ether by diazotization and reactn. with CuCl see (3).]

$\bar{C}$  on nitration with 1 pt. fuming  $\text{HNO}_3$  ( $D = 1.52$ ) at  $-10$  to  $+25^\circ$  yields (6) a product, m.p.  $81^\circ$  (6), which may have been an impure form of the trinitro cpd., 2,4,6-trinitro-3-chloroanisole, m.p.  $86^\circ$ , obtd. (61% yield (7)) by use of 5 pts. fuming  $\text{HNO}_3$  ( $D = 1.51$ ) + 5 pts. conc.  $\text{H}_2\text{SO}_4$  at  $-15^\circ$ . [The numerous possible mono- and di-nitration products of  $\bar{C}$  cannot be discussed here and, in any case, have not been reported by direct nitration of  $\bar{C}$ .]

[For a study of the reactn. kinetics of the splitting of  $\bar{C}$  in acid soln. see (8).]

3:6195 (1) Gattermann, *Ann.* 357, 319 (1907). (2) Cameron, *Am. Chem. J.* 20, 238 (1898). (3) Reverdin, Eckhard, *Ber.* 32, 2626 (1899). (4) von Auwers, *Z. physik. Chem.* A-159, 418 (1932). (5) Holleman, *Rec. trav. chim.* 37, 104 (1915). (6) Reverdin, Phillip, *Ber.* 38, 3776 (1905); *Bull. soc. chim.* (3) 33, 1322 (1905). (7) Schlubach, Mergenthaler, *Ber.* 58, 2731 (1925). (8) Ghaswalla, Donnan, *J. Chem. Soc.* 1936, 1311-1316.



3:6197 DICHLOROMALEYL (DI)CHLORIDE  $\text{Cl}$   $\text{C}_4\text{O}_2\text{Cl}_4$ Beil. II - 754  
XVII<sub>1</sub>-(138)

B.P.

192-194°

(1)

unsym.

(B)  $D_4^{20} = 1.7091$  (2) $n_{\text{D}}^{20} = 1.51947$  (2)

190° at 743 mm. (2)

sym.

86-89° at 11 mm. (3)

(A)  $D_4^{20} = 1.6723$  (2) $n_{\text{D}}^{20} = 1.51572$  (2)

[See also dichloromaleic acid (3:3634) and dichloromaleic anhydride (3:3635).]

Colorless mobile lachrymatory liq. with penetrating camphoraceous odor but *not* fuming in moist air. — Insol. aq. but volatile with steam without hydrolysis. — Soluble in org. solvents.

Although  $\bar{\text{C}}$  has not been separated into the completely pure desmotropic forms (A) and (B), their presence is clearly evidenced (2). The relative proportion of the two forms varies with the age of the sample and other conditions, but the above data on density and refraction indicate the extremes so far realized (for much further detail see (2)).

[For prepn. of ord.  $\bar{\text{C}}$  (mixture of (A) and (B)) from succinyl (di)chloride (3:6200) with  $\text{Cl}_2$  at 145° in pres. of Fe (81% yield) see (2) (note that some dichloromaleic anhydride (3:3635) is also formed, that in absence of Fe the reactn. is very slow, and that use of  $\text{I}_2$  in place of Fe lowers yield of  $\bar{\text{C}}$  to 54% (2)); from chlorofumaryl (di)chloride (8:6105) with  $\text{Cl}_2$  in pres. of Fe see (1); from dichloromaleic anhydride (3:3635) with  $\text{PCl}_5$  see (1); from dihydromfumaryl (di)chloride [Beil. II<sub>1</sub>-(303)] with  $\text{AlCl}_3$  at 100° see (3).]

Ord.  $\bar{\text{C}}$  with 60% of its wt. of  $\text{AlCl}_3$  spontaneously evolves  $\text{HCl}$ ; after further hgt. at 100° and pouring into aq. the ethereal extract yields (2) a prod. which reacts as substantially pure unsym. form (B).

Ord.  $\bar{\text{C}}$  is not affected by ord. treatment with boilg. aq. or boilg. aq. KOH (2), although it is attacked by alc. KOH (1). —  $\bar{\text{C}}$  on very protracted (168 hrs.) boilg. with aq. slowly dissolves giving (2) an acidic soln. which on extraction with ether followed by drying and evapn. of this solvent gives (80% yield) dichloromaleic anhydride (3:3635).

[For study of rate of reactn. of  $\bar{\text{C}}$  with MeOH or with aniline see (2).]

[For condens. of  $\bar{\text{C}}$  with 1-aminoanthraquinone in prepn. of dyestuffs see (2) (4).]

Ord.  $\bar{\text{C}}$  (2 g.) in  $\text{C}_6\text{H}_6$  (150 mL.) treated with 4 moles aniline (3.4 g.) in  $\text{C}_6\text{H}_6$  (30 mL.) immediately ppts. aniline hydrochloride; after stdg. for  $\frac{1}{2}$  hr., then removing this ppt., the filtrate leaves on evapn. a mixture (m.p. 165-185°; yield 67-83% (2)) of two different dianilides, which can be separated by recrystn. from hot alc.: the dianilide from the sym. dichloride (A) is *white*, has m.p. 193°, and with alc. KOH is much more slowly hydrolyzed than its isomer and during such hydrolysis shows no transient color; the dianilide from the unsym. dichloride (B) is *yellow*, has m.p. 170°, and with hot 8% alc. KOH readily hydrolyzes with development of a transient cherry-red coloration. — Note that, although the *white* dianilide is somewhat more readily sol. in hot alc. than the *yellow* isomer, it also separates first on slow cooling; note also that on hydrolysis of the anilides with alc. KOH the presence of aniline is readily detected but (presumably because of further attack by the alkali) no dichloromaleic acid can be recovered in either case.

3:6197 (1) Vandevelde, *Bull. acad. roy. Belg.* (3) 37, 680-700 (1899); *Cent.* 1900, I 404. (2) Leder, *J. prakt. Chem.* (2) 130, 255-288 (1931). (3) Ott, *Ann.* 392, 271 (1912). (4) Leder, *Ger.* 558,248, Sept. 3, 1932; *Cent.* 1932, II 3789.

## 3:6200 SUCCINYL (DI)CHLORIDE


 Beil. II - 613  
 II<sub>1</sub>-(264)  
 II<sub>2</sub>-(553)

B.P.		M.P.					
193.3°	at 760 mm. (1)	20° (7)	$D_4^{20} = 1.3748$ (9)	$n_D^{20} = 1.4683$ (9)			
190-102° cor.		18.5° (5)					
	at 760 mm. (2)						
150-152° cor.		17.7° (9)	$D_4^{15.2} = 1.3948$ (6)	$n_D^{15.2} = 1.47348$ (6)			
	at 214 mm. (2)						
114-116°	at 55 mm. (3)	17° (10)					
103-104°	at 25 mm. (4)	16-17° (4)					
95° cor.	at 20 mm. (5)						
88.8°	at 19 mm. (6)						
87-88°	at 18 mm. (7)						
95-96°	at 16 mm. (19)						
103°	at 15 mm. (8)						
78.6°	at 11 mm. (9)						

Note that  $\bar{C}$  may react in either *sym.* (above) or *unsym.* form acc. to circumstances. [For discussion of structure see (1) (5) (7) (9) (10); in the liquid only the *sym* form ( $\bar{C}$ ) exists (9).] —  $\bar{C}$  is sol. in  $\text{C}_6\text{H}_6$ , but insol. in pet. ether (7)

[For prepn. of  $\bar{C}$  from succinic acid (1.0530) with  $\text{PCl}_5$  (yield: 85% (8) (12)) (13) (14) (4) (5) see indic. refs. (note that neither  $\text{PCl}_3 + \text{ZnCl}_2$  (8) nor  $\text{SOCl}_2$  (16) give  $\bar{C}$ ); for prepn. of  $\bar{C}$  from succinic anhydride (1.0710) with  $\text{PCl}_5$  (4) (6), with  $\text{PCl}_3 + \text{Cl}_2$  (17), or with  $\text{SOCl}_2 + \text{ZnCl}_2$  at 200-240° (18) (35) see indic. refs.; for formn. of  $\bar{C}$  from the trimer of  $\beta$ -aldehydopropionic acid with  $\text{PCl}_5$  see (19) ]

[ $\bar{C}$  with  $\text{Cl}_2 + \text{Fe}$  at 145° gives (81% yield (20)) dichloromaleyl dichloride (3.6197) cf. (21),  $\bar{C}$  with  $\text{Br}_2$  yields (22) (23) mixt. of *d,l*- and *meso*- $\alpha,\alpha'$ -dibromosuccinyl dichlorides;  $\bar{C}$  with  $\text{Br}_2 + \text{Fe}$  yields (24) dibromomaleic anhydride [Beil. XVII-435, XVII<sub>1</sub>-(233)], m.p. 118°.]

[ $\bar{C}$  on reduction with  $\text{Na/Hg} + \text{AcOH}$  in ether (25) or with  $\text{H}_2 + \text{Pd}$  (25) (15) gives (54% yield (26))  $\gamma$ -butyrolactone (1.5070), b.p. 206°.]

[ $\bar{C}$  with  $\text{AlCl}_3 + \text{C}_6\text{H}_6$  yields (27)  $\gamma,\gamma$ -diphenyl- $\gamma$ -butyrolactone [Beil. XVII-367], m.p. 90° (arising from reactn. of  $\bar{C}$  in the *unsym* form), 1,2-dibenzoylthane [Beil. VII-773, VII<sub>1</sub>-(401)], m.p. 144° (arising from reactn. of the *sym.* form), and  $\beta$ -benzoylpropionic acid [Beil. X-696, X<sub>1</sub>-(330)], m.p. 116°.]

[ $\bar{C}$  on distn. or htg. with succinic acid (1.0530) (30) (31), or on htg. (31) with anhydrous oxalic acid (1.0535) or on protracted boiling with  $\text{Na}$  in xylene (32), or on htg. with diethyl succinate (1.3756) +  $\text{ZnCl}_2$  (33), yields succinic anhydride (1.0710), m.p. 120°.]

$\bar{C}$  with conc. aq.  $\text{NH}_4\text{OH}$  (7) or with  $\text{NH}_3$  gas in  $\text{C}_6\text{H}_6$  reacts mainly in the *unsym.* form (7) yielding the hygroscopic *unsym.* succindiamide [Beil. XVII-410] with at most 5% of *sym*-succindiamide, m.p. 260°;  $\bar{C}$  with aniline in  $\text{C}_6\text{H}_6$  (7) (34), however, gives 90% yield (7) *sym*-succindiamide, m.p. 230°.

[For behavior of  $\bar{C}$  with diethyl sodio-malonate see (35) (36).]

$\bar{C}$  on hydrolysis yields succinic acid (1.0530) q.v., m.p. 185°.

(1891). (5) Garner, Sugden, *J. Chem. Soc.* 1927, 2878-2880. (6) von Auwers, Schmidt, *Ber.* 46, 478 (1913). (7) Morrell, *J. Chem. Soc.* 195, 1736-1739 (1914). (8) Clark, Bell, *Trans. Roy. Soc. Can.* (3) 27, III 97-103 (1933). (9) Martin, Partington, *J. Chem. Soc.* 1939, 1170-1181. (10) Purvis, Jones, Tasker, *J. Chem. Soc.* 97, 2289 (1919).

(11) Vorländer, *Ber.* 39, 2268-2269, Note (1897). (12) Curtius, Hechtenberg, *J. prakt. Chem.* (2) 195, 302, Note (1923). (13) Gerhardt, Chiozza, *Ann.* 87, 293-304 (1853). (14) Möller, *J. prakt. Chem.* (2) 22, 298 (1880). (15) Fröschl, Maier, *Monatsh.* 59, 264-268 (1932). (16) McMaster, Ahmann, *J. Am. Chem. Soc.* 59, 149 (1937). (17) Clemmensen, Miller (to Monsanto Chemical Co.), U.S. 1,974,845, Sept. 25, 1934; *Cent.* 1935, I 969; *C.A.* 28, 7265 (1934). (18) Kyrides (to Monsanto Chem. Co.), U.S. 1,951,394, March 29, 1934; *Cent.* 1934, II 333. (19) Carrière, *Ann. chim.* (9) 17, 91 (1922). (20) Leder, *J. prakt. Chem.* (2) 139, 269-271 (1931). (21) Kauder, *J. prakt. Chem.* (2) 31, 1-39 (1895). (22) Ing. Perkin, *J. Chem. Soc.* 125, 1815, 1822 (1921).

37, 680-700; *Cent.* :

*J. prakt. Chem.* (2) :

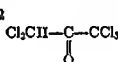
*Ann.* 629, 17 (1907)

345-348 (1888).

(31) Anschütz, *Ann.* 226, 9, 16-17 (1881). (32) Pearl, Evans, Dehn, *J. Am. Chem. Soc.* 60, 2479 (1938). (33) Kyrides, Dvornikoff, *J. Am. Chem. Soc.* 55, 4639 (1933). (34) Dunlap, Cummer, *J. Am. Chem. Soc.* 25, 621 (1903). (35) Ruggli, Maeder, *Helv. Chim. Acta* 26, 1476-1498 (1913); *C.A.* 38, 2934 (1944). (36) Ruggli, Maeder, *Helv. Chim. Acta* 29, 1499-1511 (1943); *C.A.* 38, 2935 (1944).

### 3:6205 PENTACHLOROPROPANONE-2

(Pentachloroacetone)



$\text{C}_3\text{HOC}_2\text{Cl}_5$

Beil. I - 656

I<sub>1</sub>—

I<sub>2</sub>—

B.P.

F.P.

102° at 753 mm. (1)

+2.1° (2)

$D_{15}^{15} = 1.60$  (3)

97.5-98.5° at 40 mm. (2)

$D_{15}^{15} = 1.576$  (1)

[See also hexachloropropanone-2 (3:6312).]

Colorless oil with odor suggesting chloral (3:5210); slightly sol. cold aq. (aq. at 0° dis. 0.1 vol.  $\bar{\text{C}}$  (1)) but on warming to 50-60° the soln. becomes turbid. —  $\bar{\text{C}}$  with aq. at 0° forms (1) (4) a crystn. tetrahydrate, m.p. 15-17° (4), 15° dec. (1). —  $\bar{\text{C}}$  is volatile with steam.

[For prepn. of  $\bar{\text{C}}$  from acetone (1:5400) with  $\text{Cl}_2$  in sunlight see (1); from chloroacetone (3:5425) with  $\text{Cl}_2$  at 50-70° in light see (5) cf. (3); from citric acid (1:0455) in aq. soln. at 100° with  $\text{Cl}_2$  see (1); from chloranilic acid (3:4970) in aq. with  $\text{Cl}_2$  in pres. of  $\text{I}_2$  see (6); from isopropyl alcohol (1:6135) at 65° with  $\text{Cl}_2$  see (7); for formn. of  $\bar{\text{C}}$  from citric acid, gallic acid, quinic acid, salicylic acid, iadigo, etc., by distn. with  $\text{HCl}$  +  $\text{KClO}_3$  see (4); note that in prepn. of  $\bar{\text{C}}$  some hexachloroacetone (3:6312) is frequently also obt'd.]

$\bar{\text{C}}$  with  $\text{PCl}_5$  in s.t. at 180° for 6-8 hrs. yields (8) I,1,1,2,2,3,3-heptachloropropane (3:0200) b.p. 247-248°, m.p. 30°.

$\bar{\text{C}}$  with dil. aq. KOH undergoes hydrolytic cleavage yielding (1) (3) chloroform (3:5050) and the K salt of dichloroacetic acid (3:6203).

$\bar{\text{C}}$  with anilino in dil. AcOH yields (1) (3) chloroform (3:5050) and dichloroacetanilide [Beil. XII-244, XII-1-(193)], cryst. from aq.,  $\text{C}_6\text{H}_5$ , or ether/alc., m.p. 117°. —  $\bar{\text{C}}$  with alc.  $\text{NH}_4\text{OH}$  yields (1) chloroform (3:5050) and dichloroacetamido [Beil. II-205, II-1-(92), II-1-(106)], cryst., m.p. 98°.

3:6205 (1) Cloëz, *Ann. chim.* (6) 9, 187-194 (1836). (2) Edwards, Evans, Watson, *J. Chem. Soc.* 1937, 1914-1915. (3) Fritsch, *Ber.* 29, 598 (1893); *Ann.* 279, 317-318 (1894). (4) Stadel, *Ann.* 11, 293-301 (1859). (5) I.G., French 816,950, Aug. 21, 1937; *Cent.* 1938, I 2216. (6) Levy, Jedlicka, *Ann.* 249, 87-90 (1888). (7) Bue (to Standard Oil. Co. of N.J.), U.S. 1,301,757, Sept. 27, 1921; *Cent.* 1922, IV 942. (8) Fritsch, *Ann.* 297, 314 (1897).



alm. ident. with corresp. deriv. from the isomeric ethyl  $\gamma$ -chloroacetoacetate (3:6375)); for corresp. Mg, Cu, or Ni enolates see (20).

[ $\bar{C}$  with phenols in pres. of conc.  $H_2SO_4$  or  $P_2O_5$  undergoes condensation and ring closure with loss of  $H_2O$  giving the corresp. substituted coumarins: e.g.,  $\bar{C}$  with *m*-cresol (1:1730) in conc.  $H_2SO_4$  at  $0^\circ$  gives (6) 3-chloro-4,7-dimethylcoumarin, ndls. from alc., m.p.  $135^\circ$  (6);  $\bar{C}$  with *p*-cresol (1:1410) similarly (6) (or in small yield (21) with  $P_2O_5$ ) gives 3-chloro-4,6-dimethylcoumarin, ndls. from AcOH, m.p.  $160^\circ$  (6),  $158^\circ$  (21): for corresp. reactn. of  $\bar{C}$  with  $\alpha$ -naphthol (1:1500) (22) (6), with  $\beta$ -naphthol (1:1540) (23), with 6-chloro-*m*-cresol (4-chloro-3-methylphenol) (3:1535) (24) see indic. refs. — This type of condensation also occurs with polyhydric phenols: e.g.,  $\bar{C}$  with resorcinol (1:1530) + conc.  $H_2SO_4$  at  $0^\circ$  (25) or with  $P_2O_5$  in alc. (26) gives 3-chloro-7-hydroxy-4-methylcoumarin, cryst. from alc. with  $\frac{1}{2} H_2O$  (lost at  $105-110^\circ$ ) and then melting  $236^\circ$  (25) (26); for corresp. behavior of  $\bar{C}$  with orcinol (1:1525) (22) (25), with pyrogallol (1:1555) (22) (25), see indic. refs.; many other cases are known. — Note, however, with particular care that  $\bar{C}$  with sodium salts of these phenols reacts in a different manner yielding substituted coumarone derivs. (cf. case of sodium phenolate in fifth paragraph).]

$\bar{C}$  with aq. solns. of diazonium salts behaves quite differently from the isomeric ethyl  $\gamma$ -chloroacetoacetate (3:6375): e.g.,  $\bar{C}$  in alc. with aq. benzenediazonium sulfate in pres. of NaOAc (2 moles) yields (27) (28) (4) ethyl  $\alpha$ -chloro- $\alpha$ -(phenylhydrazono)acetate [Beil. XV-270], yel. lfts. or pl. from alc., m.p.  $80-81^\circ$  (28) (4),  $70-71^\circ$  (27) (for use of this reactn. on mixts. of  $\bar{C}$  with the isomer see (4)).

$\bar{C}$  with excess hydrazine hydrate is reduced with evolution of  $N_2$  (1);  $\bar{C}$  with phenylhydrazine (2 moles) condenses and ring-closes yielding (29) (30) 4-(benzeneazo)-3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-328, XXIV-1(319)], or-red. ndls. from alc., AcOH, or  $CHCl_3$ , m.p.  $156-157^\circ$  (note, however, that in pres. of ether the reactn. with phenylhydrazine takes a different course yielding (31) ethyl  $\beta$ -(benzeneazo)-crotonate [Beil. XVI-27], red ndls. from alc., m.p.  $50-51^\circ$ ).

[ $\bar{C}$  with thioacetamide on warming yields (32) 5-carbethoxy-2,4-dimethylthiazole [Beil. XXVII-318], cryst. from ether, m.p.  $50-51^\circ$  (32). —  $\bar{C}$  with  $NH_4SCN$  (33) or better  $Ba(SCN)_2$  (34) in alc. gives (55% yield (34)) 5-carbethoxy-2-hydroxy-4-methylthiazole [Beil. XXVII-338], lfts. from alc., m.p.  $128^\circ$  (33),  $127-129^\circ$  (34); note that this prod. may be regarded as merely the isomeric ethyl  $\alpha$ -(thiocyano)acetoacetate (35). —  $\bar{C}$  with  $NH_4$  dithiocarbamate (from  $NH_4OH + CS_2$ ) in alc. eliminates  $NH_4Cl$  giving an intermediate, m.p.  $115-121^\circ$ , according to mode of htg. (38) but which on fusion ring-closes with loss of aq. to 5-carbethoxy-2-mercapto-4-methylthiazole [Beil. XXVII-339], ndls. from alc., m.p.  $150^\circ$  (38),  $141^\circ$  (39).]

[ $\bar{C}$  with urea in alc. contg. a little aq. HCl gives on stdg. 5 months (36) 5-carbethoxy-2-hydroxy-4-methylimidazole [Beil. XXV-216], ndls. from aq. or tbls. from alc., m.p.  $218^\circ$  (36). —  $\bar{C}$  (1 mole) with thiourea (1 mole) at  $90^\circ$  reacts vigorously eliminating  $H_2O$  and giving (alm. quant. yield (37)) as the hydrochloride 2-amino-5-carbethoxy-4-methylthiazole [Beil. XXVII-338]; addn. of alk. sets free the base, ndls. from ether/alc., m.p.  $175^\circ$  (37) (13).]

3:6207 (1) Macbeth, *J. Chem. Soc.* 123, 1125 (1923). (2) Allihn, *Ber.* 11, 567-570 (1878). (3) Milone, *Gazz. chim. ital.* 65, 342 (1935). (4) Favrel, Prevost, *Bull. soc. chim.* (4) 49, 243-261 (1931). (5) Haller, Held, *Bull. soc. chim.* (2) 65, 898-892 (1887). (6) Dey, *J. Chem. Soc.* 107, 1646 (1915). (7) Gault, Klees, *Bull. soc. chim.* (4) 39, 889-905 (1926); *Compt. rend.* 179, 600 (1924). (8) von Köpek-Norwall, *Ber.* 51, 393-398 (1918). (9) Mewes, *Ann.* 245, 58-60, 66-69 (1880). (10) von Meyer, *Bull. soc. chim.* (4) 1, 914-916 (1907). (11) von Meyer, *Bull. soc. chim.* (4) 1, 914-916 (1907). (12) von Meyer, von Findelsen, *Ann.* 318, 381 (1901). (13) Gault, *Gazz. chim. ital.* 22, II 40-41 (1892). (14) Favrel, *Bull. soc. chim.* (4) 1, 914-916 (1907).

{18} Genvresse, *Ann. chim.* (6) 24, 64-65 (1891). {10} Wislicenus, Stoeber, *Ber.* 35, 542-543 (1902). {20} Allihn, *Ber.* 12, 1298-1300 (1879).  
 {21} Robertson, Sandrock, *J. Chem. Soc.* 1932, 1180, 1183-1184. {22} Chakravarti, *J. Indian Chem. Soc.* 8, 407-411 (1931). {23} Dey, *J. Chem. Soc.* 107, 1629 (1915). {24} Dey, Dalal, *J. Chem. Soc.* 123, 3390 (1923). {25} von Pechmann, Hanke, *Ber.* 34, 357-360 (1901). {26} Chakravarti, *J. Indian Chem. Soc.* 8, 136 (1931). {27} Bowack, Lapworth, *J. Chem. Soc.* 87, 1859 (1905). {28} Favrel, *Compt. rend.* 134, 1313 (1902). {29} Schönbrodt, *Ann.* 253, 188-193 (1889). {30} Buchka, Sprague, *Ber.* 22, 2548-2550 (1880).  
 {31} Bender, *Ber.* 20, 2747-2752 (1887). {32} Hantzsch, *Ann.* 250, 269 (1888). {33} Hantzsch, Weber, *Ber.* 20, 3131-3132 (1887). {34} Zureher, *Ann.* 250, 282-283 (1888). {35} Wohmann, *Ann.* 259, 298 (1890). {36} Behrend, *Ann.* 229, 16 (1885). {37} Zureher, *Ann.* 250, 289-290 (1888). {38} Levi, *Gazz. chim. ital.* 61, 723-724 (1931). {39} Molati, *Gazz. chim. ital.* 23, I 577 (1893). {40} Ubaldini, *Chimica e industria* (Italy) 25, 113-114 (1943); *Cent.* 1943, II 1951; *C.A.* 38, 5799 (1944).

## 3:6208 DICHLOROACETIC ACID



Beil. II - 202

 $\Pi_1$ -(90) $\Pi_2$ -(194)

B.P.		M.P.			
195°	(1) (62)	13.25° (17)	$D_4^{25} = 1.5579$	(28)	
194.5-195°	(2)	13.00° (18)			
194.42° at 760 mm.	(3)	12.15° (17)	$D_{25}^{25} = 1.5604$	(4)	
194.0-194.5° cor.	(4)	11° (19) (20)			
194°	(5) (6)	10.85° (21)	$D_{12}^{22} = 1.5594$	(14)	$n_D^{25} = 1.4650$ (8)
193.5-193.9°	(7)	19.8° (22)			
192.5° at 763 mm.	(28)	10° (23)	$D_4^{20} = 1.5648$	(28)	$n_D^{20} = 1.46582$ (27)
			1.5642	(27)	
192-103° cor., dec.	(8)	9.7° (24)	1.5634	(8)	
			(25)		
191° at 760 mm.	(9)	5-6° (14)			
190°	(10)	-4.1° (24)	$D_{20}^{20} = 1.5666$	(8)	
189-191°	(11)	-4° (26)			
		See Note 2.	$D_4^{19} = 1.5691$	(29)	$n_D^{19} = 1.4967$ (29)
			$D_4^{15} = 1.5717$	(28)	
			$D_{15}^{15} = 1.5797$	(27)	
			See Note 3.		See Note 3.
144° at 164 mm.	(12)				
149° at 142 mm.	(12)				
129° at 88 mm.	(12)				
125° at 71 mm.	(12)				
111.5° at 36 mm.	(12)				
105° at 25 mm.	(13)				
102.5° at 24 mm.	(12)				
99° at 21 mm.	(12)				
102° cor. at 20 mm.	(8) (14)				
102° u.c. at 20 mm.	(16)				
95-96° at 17 mm.	(8)				
91-92° at 12 mm.	(15)				
See Note 1.					

Note 1. The b.p. of  $\tilde{\text{C}}$  at normal press. is not very significant, some decomn to dichloroacetyl chloride (3:5290), phosgene (3:5000), and tarry products always occurring (8).

Note 2.  $\tilde{\text{C}}$  apparently can exist in at least two crystn. modifications (24); no clear-cut study of the matter, however, has been reported.

Note 3. For values of  $D_{20}^{20}$  and  $n_D^{20}$  for aq. solns. of  $\tilde{\text{C}}$  see (27).

[See also chloroacetic acid (3:1370) and trichloroacetic acid (3:1150).]

$\tilde{\text{C}}$  when pure is a colorless liq. which does not fume in moist air and which dissolves in

alm. ident. with corresp. deriv. from the isomeric ethyl  $\gamma$ -chloroacetoacetate (3:6375)); for corresp. Mg, Cu, or Ni enolates see (20).

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$\bar{C}$  with excess hydrazine hydrate is reduced with evolution of  $N_2$  (1);  $\bar{C}$  with phenylhydrazine (2 moles) condenses and ring-closes yielding (29) (30) 4-(benzeneazo)-3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-328, XXIV-1-(319)], or.-red. ndls. from alc., AcOH, or  $CHCl_3$ , m.p.  $156$ – $157^\circ$  (note, however, that in pres. of ether the reactn. with phenylhydrazine takes a different course yielding (31) ethyl  $\beta$ -(benzeneazo)-crotonate [Beil. XVI-27], red ndls. from alc., m.p.  $50$ – $51^\circ$ ).

[ $\bar{C}$  with thioacetamide on warming yields (32) 5-carbethoxy-2,4-dimethylthiazole [Beil. XXVII-318], cryst. from ether, m.p.  $50$ – $51^\circ$  (32). —  $\bar{C}$  with  $NH_4SCN$  (33) or better  $Bu(SCN)_2$  (34) in alc. gives (55% yield (34)) 5-carbethoxy-2-hydroxy-4-methylthiazole [Beil. XXVII-338], lfts. from alc., m.p.  $128^\circ$  (33),  $127$ – $129^\circ$  (34); note that this prod. may be regarded as merely the isomeric ethyl  $\alpha$ -(thiocyano)acetoacetate (35). —  $\bar{C}$  with  $NH_4$  dithiocarbamate (from  $NH_4OH$  +  $CS_2$ ) in alc. eliminates  $NH_4Cl$  giving an intermediate, m.p.  $115$ – $121^\circ$ , according to mode of htg. (38) but which on fusion ring-closes with loss of aq. to 5-carbethoxy-2-mercapto-4-methylthiazole [Beil. XXVII-339], ndls. from alc., m.p.  $150^\circ$  (38),  $141^\circ$  (39).]

[ $\bar{C}$  with urea in alc. contg. a little aq. HCl gives on stdg. 5 months (36) 5-carbethoxy-2-hydroxy-4-methylimidazole [Beil. XXV-216], ndls. from aq. or tbls. from alc., m.p.  $218^\circ$  (36). —  $\bar{C}$  (1 mole) with thiourea (1 mole) at  $90^\circ$  reacts vigorously eliminating  $H_2O$  and giving (alm. quant. yield (37)) as the hydrochloride 2-amino-5-carbethoxy-4-methylthiazole [Beil. XXVII-338]; addn. of alk. sets free the base, ndls. from ether/alc., m.p.  $175^\circ$  (37) (13).]

3:6207 (1) Macbeth, *J. Chem. Soc.* 123, 1125 (1923). (2) Allihn, *Ber.* 11, 567–576 (1878). (3) Milone, *Gazz. chim. ital.* 63, 312 (1933). (4) Favrel, Prevost, *Bull. soc. chim.* (4) 49, 213–281 (1931). (5) Haller, *Held. Bull. soc. chim.* (2) 65, 888–892 (1887). (6) Dey, *J. Chem. Soc.* 107, 1646 (1915). (7) Gault, Klees, *Bull. soc. chim.* (4) 39, 889–905 (1920); *Compt. rend.* 179, 600 (1924). (8) von Köpck-Norwall, *Ber.* 51, 393–398 (1918). (9) Mewes, *Ann.* 245, 58–60, 66–69 (1888). (10) Schönbrodt, *Ann.* 253, 170–174 (1889).

— 364 (1936). (12) von Meyer, von Findeisen, *Mend. Schreiber, Ann.* 318, 381 (1901). (14) *Gazz. chim. ital.* 22, II 40–41 (1892). (16) *sagae, Bull. soc. chim.* (4) 1, 914–916 (1907).

{15} Genyresse, *Ann. chim.* (6) **24**, 64-65 (1891). {19} Wislicenus, Stoeber, *Ber.* **35**, 542-543 (1902). {20} Allihn, *Ber.* **12**, 1298-1300 (1879).  
 {21} Robertson, Sandrock, *J. Chem. Soc.* **1932**, 1180, 1183-1184. {22} Chakravarti, *J. Indian Chem. Soc.* **8**, 407-411 (1931). {23} Dey, *J. Chem. Soc.* **1915**, 1629 (1915). {24} Dey, Dalal, *J. Chem. Soc.* **123**, 3390 (1923). {25} von Pechmann, Hanke, *Ber.* **34**, 357-360 (1901). {26} Chakravarti, *J. Indian Chem. Soc.* **8**, 136 (1931). {27} Bowack, Lapworth, *J. Chem. Soc.* **87**, 1859 (1905). {28} Favrel, *Compt. rend.* **134**, 1313 (1902). {29} Schönbrodt, *Ann.* **253**, 188-193 (1899). {30} Buchka, Sprague, *Ber.* **27**, 2548-2550 (1890).  
 {31} Bender, *Ber.* **20**, 2747-2752 (1887). {32} Hantzsch, *Ann.* **250**, 269 (1888). {33} Hantzsch, Weber, *Ber.* **20**, 3131-3132 (1887). {34} Zürcher, *Ann.* **250**, 282-283 (1888). {35} Wohmann, *Ann.* **259**, 298 (1890). {36} Behrend, *Ann.* **279**, 16 (1885). {37} Zürcher, *Ann.* **250**, 289-290 (1888). {38} Levi, *Gazz. chim. ital.* **61**, 723-724 (1931). {39} Mielati, *Gazz. chim. ital.* **23**, I 577 (1893). {40} Ubaldini, *Chimica e industria* (Italy) **25**, 113-114 (1943), *Cent.* **1943**, II 1051; *C.A.* **38**, 5799 (1944).

## 3:6208 DICHLOROACETIC ACID



Beil. II - 202

II-(90)

II-(194)

B.P.		M.P.			
195°	{1} {62}	13.25° {17}	$D_4^{25} = 1.5579$	{28}	
194.5-195°	{2}	13.00° {18}			
194.42° at 760 mm.	{3}	12.15° {17}	$D_{25}^{25} = 1.5604$	{4}	
194.0-194.5° cor.	{4}	11° {19} {20}			
194°	{5} {6}	10.85° {21}	$D_{22}^{22} = 1.5594$	{14}	$n_D^{22} = 1.4659$ {8}
193.5-193.9°	{7}	10.8° {22}			
192.5° at 763 mm.	{28}	10° {23}	$D_4^{20} = 1.5648$	{28}	$n_D^{20} = 1.46582$ {27}
				{28}	1.5642 {27}
192-193° cor., dec.	{8}	9.7° {24}	1.5634	{8}	
				{25}	
191° at 760 mm.	{9}	5-6° {14}			
190°	{10}	-4.1° {24}	$D_{20}^{20} = 1.5666$	{8}	
189-191°	{11}	-4° {26}			
			See Note 2.	$D_4^{19} = 1.5691$	{29}
				$D_4^{15} = 1.5717$	{28}
				$D_{15}^{15} = 1.5707$	{27}
				See Note 3.	See Note 3.
144° at 164 mm.	{12}				
140° at 142 mm.	{12}				
120° at 88 mm.	{12}				
125° at 71 mm.	{12}				
111.5° at 36 mm.	{12}				
105° at 25 mm.	{13}				
102.5° at 24 mm.	{12}				
99° at 21 mm.	{12}				
102° cor. at 20 mm.	{8} {14}				
102° u.c. at 20 mm.	{16}				
95-96° at 17 mm.	{8}				
91-92° at 12 mm.	{15}				
See Note 1.					

Note 1. The b.p. of  $\bar{C}$  at normal press. is not very significant, some decompn. to dichloroacetyl chloride (3:5290), phosgene (3:5900), and tarry products always occurring (8).

Note 2.  $\bar{C}$  apparently can exist in at least two crystn. modifications (24); no clear-cut study of the matter, however, has been reported.

Note 3. For values of  $D_{20}^{20}$  and  $n_D^{20}$  for aq. solns. of  $\bar{C}$  see (27).

[See also chloroacetic acid (3:1370) and trichloroacetic acid (3:1150).]

$\bar{C}$  when pure is a colorless liq. which does not fume in moist air and which dissolves in



aq. without opalescence. — Ordinary comml. samples of  $\bar{C}$  may contain also chloroacetic acid (3:1370) and trichloroacetic acid (3:1150) as well as decompn. products from these or from  $\bar{C}$  itself, cf. (30) (31).

### MISCELLANEOUS PHYSICAL PROPERTIES OF $\bar{C}$

Adsorption of  $\bar{C}$ . [For studies of adsorption of  $\bar{C}$  by activated carbon, charcoal, etc., see (32) (33) (34) (35) (36) (39); by silica gel see (33); by cellulose (viscose) see (37); by hide powder see (38).]

Distribution of  $\bar{C}$  between solvents. [For studies and data on distribution of  $\bar{C}$  between aq. + ether at 25° (40) (41); aq. +  $C_6H_6$  at 15° (42) (43) (44) (45); aq. + nitrobenzene (43); aq. + toluene (43); aq. + *o*-nitrotoluene (43) (47); aq. +  $CHCl_3$  (3:5050) (43); aq. +  $CCl_4$  (3:5100) (43) (46); aq. +  $EtBr$  (43) (46); aq. (contg.  $MgSO_4$ ) + *di*-*n*-butyl ether (1:7950) (48); aq. + olive oil (49); acetone + glycerol (50) see indic. refs.]

Binary systems contg.  $\bar{C}$ . [For f.p./compn. data on systems  $\bar{C}$  + trichloroacetic acid (3:1150) (25);  $\bar{C}$  +  $AcOH$  (1:1010) (25);  $\bar{C}$  + crotonic acid (1:0425) (25);  $\bar{C}$  + benzoic acid (1:0715) (25);  $\bar{C}$  + *o*-toluic acid (1:0690) (25);  $\bar{C}$  + *m*-toluic acid (1:0705) (25);  $\bar{C}$  + *p*-toluic acid (1:0795) (25);  $\bar{C}$  + phenylacetic acid (1:0665) (25);  $\bar{C}$  + cinnamic acid (1:0735) (25);  $\bar{C}$  + 2,6-dimethylpyrone (24);  $\bar{C}$  + azobenzene (19);  $\bar{C}$  + urea (51);  $\bar{C}$  + ethyl carbamate (urethane) (51) see indic. refs.]

### PHYSIOLOGICAL BEHAVIOR OF $\bar{C}$

[For study of toxicity of  $\bar{C}$  see (52); for action of  $\bar{C}$  on human skin see (53) (54).]

### PREPARATION OF $\bar{C}$

#### FROM VARIOUS CHLORO COMPOUNDS

From chloral hydrate. [For prepn. of  $\bar{C}$  from chloral hydrate (3:1270) with aq.  $NaCN$  +  $CaCO_3$  (yields: 88–92% (55), 90% (15)) or with aq.  $NaCN$  (60–65% yield (16)) or with  $K_3Fe(CN)_6$  (63) see indic. refs.; cf. also (56) (57); note here also the closely related matter of conversion of anhydrous chloral (3:5210) with alcohols +  $KCN$  (58) to the corresponding alkyl dichloroacetates, e.g., with  $MeOH$  to methyl dichloroacetate (3:5655) or with  $EtOH$  to ethyl dichloroacetate (3:5850), etc.; also conversion of chloral hydrate (3:1270) in ether with  $KCN$  + conc. aq.  $NH_4OH$  to (65–78% yield (59)) cf. (58)  $\alpha,\alpha$ -dichloroacetamide (see also below).]

From trichloroacetic acid. [For prepn. of  $\bar{C}$  from trichloroacetic acid (3:1150) by partial reduction with  $Zn$  + aq. (13), with  $Cu$  powder in aq. (80% yield (14)) or  $C_6H_6$  + aniline (75–85% yield (8)) cf. (60), or by electrolytic reduction (80% yield (61)) see indic. refs.]

From chloroacetic acid. [For prepn. of  $\bar{C}$  from chloroacetic acid (3:1370) with  $Cl_2$  (1), or  $Cl_2$  in pres. of  $I_2$  (62), see indic. refs.]

From dichloroacetaldehyde. [For prepn. of  $\bar{C}$  from dichloroacetaldehyde (3:5180) by oxidn. with  $HNO_3$  see (2).]

From other misc. chloro compounds. [For formn. of  $\bar{C}$  from ethyl dichloroacetate (3:5850) with  $HCl$  gas (100% yield (11)); from dichloroacetyl chloride (3:5290) by hydrolysis or by disproportionation with  $AcOH$  (acetyl chloride (3:7065) also being formed (64)); from  $\beta,\beta,\beta$ -trichloro- $\alpha$ -hydroxypropionic acid (trichlorolactic acid) [Beil. III-286, III<sub>1</sub>-(111), III<sub>2</sub>-(210)] or its ethyl ester with excess aq.  $Ba(OH)_2$  (65); from  $\beta,\beta$ -dichloro- $\alpha$ -acetoxyacrylonitrile [Beil. III<sub>1</sub>-(135), III<sub>2</sub>-(254)] with boilg. aq. (66) or from  $\alpha,\beta,\beta$ -trichloro- $\alpha$ -acetoxypropionitrile [Beil. III-288, III<sub>1</sub>-(112)] with 33%  $H_2SO_4$  (66); from 2,2,4,4,6,6-hexachlorocyclohexantrione-1,3,5 (hexachlorophloroglucinol) [Beil. VII-854,

VII<sub>1</sub>-(469)] with aq. (*sym*-tetrachloroacetone (3:6050) is also formed) (67); from *unsym*-dichloroacetone (3:5430) by oxidn. with  $\text{HNO}_3$  + air (68); from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) with air in ultra-violet light in pres. of water (21) cf. (69); from pentachloroethane (3:5880) by partial hydrolysis with 88-97%  $\text{H}_2\text{SO}_4$  at 168° (90% yield (70)) see indic. refs.]

From miscellaneous non-chlorinated compounds. [For formn. of  $\bar{\text{C}}$  from AcOH with  $\text{Cl}_2$  (71) in presence of  $\text{I}_2$  (62) see indic. refs.; from acetylene with  $\text{HOCl}$  at 75-80° see (72); from ethyl acetoacetate (1:1710) with aq. bleaching powder (yield 60%) see (73); from phloroglucinol (1:1620) with aq.  $\text{Cl}_2$  see (74) (75); from pyrrole with  $\text{NaOCl}$  see (76).]

## CHEMICAL BEHAVIOR OF $\bar{\text{C}}$

### BEHAVIOR AS AN ACID

Acid strength of  $\bar{\text{C}}$ .  $\bar{\text{C}}$  in aq. soln. is a strong acid [ionization const. at 25° is  $K = 5.14 \times 10^{-2}$  (77) cf. (78) (18), at 18°  $K = 5.15 \times 10^{-2}$  (45); for studies of activity coefficient of  $\bar{\text{C}}$  in aq. and in salt solns. see (18) (48). — For tests on corrosion of metals by  $\bar{\text{C}}$  see (16)].

[Studies of acid strength of  $\bar{\text{C}}$  in other solvents include the following: in aq. MeOH (70) (81), in aq. EtOH (79) (80), in abs. EtOH (82), in *n*-BuOH (5) (83), in  $\text{C}_6\text{H}_6$  (84), in chlorobenzene (85), in formamide (86), in acetonitrile (87).]

$\bar{\text{C}}$  on titration gives Neut. Eq. = 129.

Salts of  $\bar{\text{C}}$ . This topic cannot be exhaustively treated here but following examples are cited.

Salts with inorganic bases. [ $\text{NH}_4\bar{\text{A}}$  (88); hydroxylamine salt,  $\text{HONH}_2\bar{\text{A}}$ , cryst. from  $\text{C}_6\text{H}_6/\text{EtOH}$ , m.p. 116.0-116.5° (89);  $\text{Na}\bar{\text{A}}$  (on electrolysis gives (90)  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and also (91) dichloromethyl dichloroacetate,  $\text{K}\bar{\text{A}}$ , lfts. from alc. (11), on dry distn. gives (92)  $\bar{\text{C}}$  +  $\text{KCl}$  +  $\text{CO}_2$  + carbon,  $\text{Ca}\bar{\text{A}}_2$ , ndls. from abs. alc. (93);  $\text{Ca}\bar{\text{A}}_2 \cdot 3\text{H}_2\text{O}$  (93);  $\text{Cu}\bar{\text{A}}_2$  (88);  $\text{Cu}\bar{\text{A}}_2 \cdot 4\text{H}_2\text{O}$  (88);  $\text{Cd}\bar{\text{A}}_2 \cdot \text{H}_2\text{O}$  (94);  $\text{Mn}\bar{\text{A}}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  (94);  $\text{Co}\bar{\text{A}}_2 \cdot 3\text{H}_2\text{O}$  (94); note that all the foregoing salts are sol. nq.]

[Inorg. salts of  $\bar{\text{C}}$  which are sparingly sol. aq. include the following:  $\text{Ag}\bar{\text{A}}$  (93);  $\text{Th}(\text{OH})_2\bar{\text{A}}_2$  (96);  $(\text{UO})\bar{\text{A}}_2 \cdot 2\text{H}_2\text{O}$  (97).]

Salts with organic bases (amines). [Aniline dichloroacetate, m.p. 122-123° (8) (98) cf. (30) (159) (note that this prod. or its components at 140° for 24 hrs. gives (98) dichloroacetanilide, m.p. 118°). — *o*-Toluidine dichloroacetate, m.p. 132.5° (98), 140° (99) (note that this prod. or its components at 140° for 18 hrs. gives (98) dichloroaceto-*o*-toluidide, m.p. 133°, but depressing m.p. of the salt to as low as 112°). — *p*-Toluidine dichloroacetate, m.p. 138° (98) (note that this prod. or its components on htg. gives (98) dichloroaceto-*p*-toluidide, m.p. 154°). — Piperazine bis-(dichloroacetate), m.p. 181° cor. (100). — Semi-carbamide dichloroacetate, m.p. 108° (101). — For salts of  $\bar{\text{C}}$  with other org. amines see (30) (99).]

Esterification of  $\bar{\text{C}}$ . [For this see the text of methyl dichloroacetate (3:5655), ethyl dichloroacetate (3:5850), *n*-propyl dichloroacetate (3:6000), isopropyl dichloroacetate (3:5890); for study of direct esterification of  $\bar{\text{C}}$  with various butyl and amyl alcs. without cat. see (102).]

Conversion of  $\bar{\text{C}}$  to corresp. acid chloride.  $\bar{\text{C}}$  with  $\text{PCl}_3$  (103), with  $\text{HCl}$  gas +  $\text{P}_2\text{O}_5$  (104), with  $\text{SOCl}_2$  (poor yield apparently due to much formn. of dichloroacetic acid anhydride (3:6430) (105) (106) (107) (108)), with  $\text{BzCl}$  (3:6240) (73% yield (111)), or with benzotrichloride (3:6540) (109) (110) gives dichloroacetyl chloride (3:5290), b.p. 108°.

Addition reactions of  $\bar{\text{C}}$  with org. cpds.  $\bar{\text{C}}$  in pres. of suitable cat. adds to olefins yielding corresp. esters [e.g.,  $\bar{\text{C}}$  with propylene +  $\text{BF}_3$  as directed gives (39.5% yield (112)) isopropyl dichloroacetate (3:5890);  $\bar{\text{C}}$  with 2-methylbutene-2 (trimethylethylene) (1:8220) at 18°

shows slight tendency toward formn. of corresp. ester in  $C_6H_6$ ,  $CHCl_3$  or  $CS_2$  but none in alc. or ether (113)].

[ $\bar{C}$  with ethylene oxide (1:6105) in dry ether at  $0^\circ$  gives (15% yield (114)) cf. (115)  $\beta$ -hydroxythyl dichloroacetate (3:9107).]

#### BEHAVIOR OF $\bar{C}$ AS DICHLORO COMPOUND

**Reduction.** [ $\bar{C}$  in alc. KOH soln. with  $H_2$  + Pd/ $CaCO_3$  splits off all its halogen as HCl (116). —  $\bar{C}$  with Zn + water on hgt. is slowly reduced to chloroacetic acid (3:1370) but reaction is much less energetic than that of trichloroacetic acid (3:1150) under same conditions (13).]

**Hydrolysis of halogen atoms of  $\bar{C}$  or its salts.** [ $\bar{C}$  with aq. in s.t. at  $100^\circ$  is slowly or in pres. of NaOH or  $Ba(OH)_2$  rapidly decomposed (93) cf. (117). — For study of kinetics of hydrolysis of  $\bar{C}$  see (118) (119). — Note, however, that  $Ag\bar{A}$  on hgt. with aq. (93), or  $\bar{C}$  (or its salts) on hydrolysis at elevated temp. and press. (120), or salts of  $\bar{C}$  htd. with aq. solns. of NaOAc or NaOBz (121), gives glyoxylic acid,  $OHC-COOH$  [Beil. III-594, III<sub>1</sub>-207, III<sub>2</sub>-(385)], m.p.  $98^\circ$ , very sol. aq. — For a method of detn. of  $\bar{C}$  in pres. of chloroacetic acid (3:1370) and trichloroacetic acid (3:1150) based on this hydrolysis see (122).]

**Behavior of  $\bar{C}$  with alkoxides.** [ $\bar{C}$  (as  $K\bar{A}$ ) with excess MeOH/NaOMe refluxed under  $H_2$ , and the solution then further esterified with MeOH/HCl, gives (62% yield (123)) cf. (124) methyl dimethoxyacetate, b.p.  $60-61^\circ$  at 12 mm.,  $D_4^{18} = 1.0962$ ,  $n_D^{18} = 1.4015$  (124); this ester upon alk. hydrolysis gives (85.7% yield (124)) dimethoxyacetic acid (glyoxylic acid dimethylacetal) as a sirup.]

[ $\bar{C}$  with excess EtOH/NaOEt under reflux followed by acidification and esterification as above gives (50% yield (125)) (126) ethyl diethoxyacetate [Beil. III-601, III<sub>1</sub>-(210), III<sub>2</sub>-(389)], b.p.  $199^\circ$  (127),  $94-98^\circ$  at 19 mm. (125),  $83-85^\circ$  at 13 mm. (125).]

[ $\bar{C}$  in excess EtOH/NaOEt with Na phenolate refluxed 14 hrs., then acidified and esterified as above, gives (61% yield (128)) ethyl diphenoxyacetate [Beil. VI-170], oil, b.p.  $240^\circ$  at 53 mm. (129),  $166-168^\circ$  at 0.8 mm. (128). — However,  $\bar{C}$  with phenol in aq. NaOH on hgt. and acidification gives (130) (131) diphenoxyacetic acid, ndls. from pet. ether or aq. AcOH, m.p.  $91^\circ$  (129) (130).]

**Condensation with hydrocarbons.** [ $\bar{C}$  with aromatic hydrocarbons on hgt. condenses with elimination of 2 HCl giving diarylacetic acids [e.g.,  $\bar{C}$  with naphthalene at  $180^\circ$  for 60-100 hrs. gives (132) di-( $\alpha$ -naphthyl)acetic acid [Beil. IX-720, IX<sub>1</sub>-(313)], cryst. from  $CCl_4$ , m.p.  $224^\circ$  (133),  $223^\circ$  u c. (134); for analogous behavior of  $\bar{C}$  with other hydrocarbons see (132)].

**Behavior of  $\bar{C}$  with  $RMgX$  compounds.** [ $\bar{C}$  with  $C_6H_5MgBr$  (large excess) in ether soln. followed by usual hydrolysis gives (34% yield (135))  $\alpha,\alpha,\beta$ -triphenylethylene glycol, ndls. from  $C_6H_6$ , m.p.  $163^\circ$  (135).]

**Behavior of  $\bar{C}$  with hydroxylamine.** [ $\bar{C}$  (1 mole) with  $NH_2OH \cdot HCl$  (1 mole) + aq. KOH (4 moles) at  $60^\circ$  for 4 hrs. gives (136) isonitrosoacetic acid (glyoxylic acid oxime) [Beil. III-599, III<sub>1</sub>-(208), III<sub>2</sub>-(389)], cryst. from dry ether, m.p.  $138^\circ$  (136) (note that this prod. forms with water a monohydrate, m.p. about  $70^\circ$  (137)).]

**Behavior of  $\bar{C}$  with aromatic amines.** (See also salt formation above.)

**With aniline.** The products of reaction of  $\bar{C}$  on hgt. with aniline are disputed [on one hand  $\bar{C}$  (1 mole) with aniline (4 moles) at  $100^\circ$ , then evapd. with NaOAc, is claimed (138) (139) to give 4,4'-diaminodiphenylacetic acid [Beil. XIV-540, XIV<sub>1</sub>-(625)], m.p. about  $195^\circ$  (140); on the other hand, the prod. is regarded by some (141) (142) as a mixt. of two stereoisomeric forms of 2,2'(?)-diaminostilbene- $\alpha,\alpha'$ -dicarboxylic acids [Beil. XIV-573]].

**With o-toluidine.** [ $\bar{C}$  (1 mole) with o-toluidine (4 moles) at  $100^\circ$  gives (140) (143) 4,4'-diamino-3,3'-dimethyldiphenylacetic acid [Beil. XIV-543, XIV<sub>1</sub>-(627)], ndls. from alc.,

m.p. 239-240° (143) dec. (140), accompanied by some 7-methylisatin-3-(*o*-tolylimide) [Beil. XXI-512], yel. lfts. from alc., m.p. about 225° dec. (138).]

With *p*-toluidine.  $\bar{C}$  (1 mole) with *p*-toluidine (4 moles) at 100° in aq. or alc. soln. gives (144) (145) 5-methylisatin-3-(*p*-tolylimide) [Beil. XXI-510, XXI-401], golden-yel. ndls. or lfts. from alc., m.p. 259° (144) (145).]

Behavior of  $\bar{C}$  with urea.  $\bar{C}$  with urea (2 moles) in pres. of NaOEt condenses to give (146) 5-ureidohydantoin (allantoin) [Beil. XXV-474, XXV-1-(692)], m.p. by ord. htg. in cap. tube is 228-230° (147), by rap. htg. in bath already at 228° is 233-234° (147).

Behavior of  $\bar{C}$  with arylhydrazines.  $\bar{C}$  with arylhydrazines in alc. KOH yields a mixt. of the two stereoisomeric arylhydrazones of glyoxylic acid [e.g.,  $\bar{C}$  with phenylhydrazine in dil. alc. KOH refluxed 2 hrs. gives (148) a mixt. of the  $\alpha$ -glyoxylic acid phenylhydrazone, m.p. abt. 135° with decompn. at 142-143°, and the  $\beta$ -glyoxylic acid phenylhydrazone, m.p. 128-129° dec. (rap. htg.) (148); for analogous behavior of  $\bar{C}$  with other arylhydrazines see (148)].

② Color test with  $NH_4OH/Cu_2Cl_2$  reagent.  $\bar{C}$  on shaking in filled stoppered bottle with conc. aq.  $NH_4OH$  contg.  $Cu_2Cl_2$  gives dark blue color within 3 min. (149); note, however, that the same behavior is shown by trichloroacetic acid (3:1150).

— Methyl dichloroacetate: oil, b.p. 143° (see 3:5655).

— Ethyl dichloroacetate: oil, b.p. 155° (see 3:5850).

— Benzyl dichloroacetate: oil, b.p. 179° at 60 mm. (150). [From  $\bar{C}$  with benzyl alcohol (1:6480) with  $HCl$  gas (150).]

— Phenyl dichloroacetate [Beil. VI-153, VI-1-(87)]: m.p. 48° (151), b.p. 247.5° cor. (151) [From dichloroacetyl chloride (3:5290) +  $AlCl_3$  in  $CS_2$  (prod. m.p. 33° was probably impure (152)).]

— *p*-Tolyl dichloroacetate: m.p. 58° (151). [Prepd. indirectly from  $\alpha,\beta$ -dichlorovinyl ethyl ether (3:5440) with *p*-cresol (1:1410) (151).]

— *p*-Nitrobenzyl dichloroacetate: oil, unsuitable as ② (160) (161).

— Phenacyl dichloroacetate: oil (153).

— *p*-Chlorophenacyl dichloroacetate: m.p. 93.0-93.8° (153).

— *p*-Bromophenacyl dichloroacetate: m.p. 98.2-99.3° (153).

— *p*-Iodophenacyl dichloroacetate: unreported.

— *p*-Phenylphenacyl dichloroacetate: unreported.

③ *S*-Benzylthiuronium dichloroacetate: m.p. 178-179° (154). [Note that for corresp. salts from chloroacetic acid (3:1370) and from trichloroacetic acid (3:1150) the values are respectively 159-160° and 148-149° (154).]

— *S*-(*p*-Chlorobenzyl)thiuronium dichloroacetate: unreported.

— *S*-(*p*-Bromobenzyl)thiuronium dichloroacetate: unreported.

—  $\alpha,\alpha$ -Dichloroacetamide: cryst. from  $C_6H_6$ , m.p. 99.4° (155), 98.5-99° (58), 98.5° (156), 97.5-99.5° (59). [From ethyl dichloroacetate (3:5850) with aq.  $NH_4OH$  (155) or in other indirect ways, e.g., from chloral ammonia with KCN + aq.  $NH_4OH$  (93% yield (58)), or from chloral hydrate (3:1270) with KCN + aq.  $NH_4OH$  (65-78% yield (59)).] — [Note that dichloroacetamide forms with bromo-chloro-acetamide or with chloro-iodo-acetamide an unbroken series of mixed crystals.]

④  $\alpha,\alpha$ -Dichloroacetanilide: colorless ndls. from alc. or by sublimation, m.p. 118° (98), 117.7° (156). [From  $\bar{C}$  with aniline at 140° for 24 hrs. (98) or from dichloroacetyl chloride (3:5290) with aniline in  $C_6H_6$  (157) or acetone (157).] — [Note that this prod. forms with  $\alpha$ -bromo- $\alpha$ -chloroacetanilide, m.p. 116.8° (157), a series of mixed cryst. and with  $\alpha$ -chloro- $\alpha$ -iodoacetanilide, m.p. 142.3°, a eutectic, m.p. 105.2° (157).] — [Note also that aniline dichloroacetate (see also above) has m.p. 122-123° (98).]

⑤  $\alpha,\alpha$ -Dichloroacet-*o*-toluidide: cryst. from 50% alc. or by sublimation, m.p. 133° (98). [From  $\bar{C}$  + *o*-toluidine at 140° for 18 hrs. (98); note that the salt *o*-toluidine dichloroacetate has same m.p. 132.5° as the  $\alpha,\alpha$ -dichloroacet-*o*-toluidide but that the m.p. of a mixture of the two compds. is depressed to below 112° (98).]

—  $\alpha,\alpha$ -Dichloroacet-*p*-toluidide: pl. from alc. or by sublimation, m.p. 154° (98). [From  $\bar{C}$  + *p*-toluidine at 148° for 18 hrs. (98); note that the corresp. salt, *p*-toluidine dichloroacetate, has m.p. 138° (98).]

—  $\alpha,\alpha$ -Dichloroacet-*N*-benzylamide: m.p. 96.2° (156), 94.8–95.6° cor. (158), 94.2–95.0° u.c. (158). [From ethyl dichloroacetate (3:5850) (158) cf. (162) or dichloroacetyl chloride (3:5290) (156) with benzylamine; note, however, that the corresp. derivs. from chloroacetic acid (3:1370) and from trichloroacetic acid (3:1150) have almost the same m.p.'s, viz., 93.0–93.6° cor. and 93.6–94.4° cor., respectively (158).]

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— TRICHLOROACETIC ACID  $\text{Cl}_3\text{C.COOH}$   $\text{C}_2\text{HO}_2\text{Cl}_3$  Beil. II - 200  
 II<sub>1</sub>-(92)  
 II<sub>2</sub>-(190)

B.P. 190°

M.P. 57°

See 3:1150. Division A: Solids.

3:6210 ACETALDEHYDE bis-(β-CHLOROETHYL)ACETAL  $\text{C}_6\text{H}_{12}\text{O}_2\text{Cl}_2$  Beil. S.N. 70  
 $\text{CH}_3\text{CH}(\text{O.CH}_2\text{CH}_2\text{Cl})_2$   
 (α,α-bis-(β-Chloroethoxy)ethane)

B.P. 104-190° dec. (2)  $D_{16}^{10} = 1.1712$  (2)  $n_D^{10.2} = 1.4532$  (2)  
 100-110° at 30 mm. (1)  
 100-108° at 17 mm. (2)  
 100-107° at 14 mm. (3)

Colorless liq. with odor resembling dichloroacetaldehyde diethylacetal (3:6110).

[For prepn. of  $\bar{C}$  from ethylene chlorohydrin (3:5552) with acetaldehyde (1:0100) + dry HCl (36% yield (2)) see (2) (1); with acetylene +  $\text{BF}_3$  (71% yield) see (3).]

3:6210 (1) Street, Adkins, *J. Am. Chem. Soc.* 50, 162-167 (1928). (2) Grignard, Purdy, *Bull. soc. chim.* (4) 31, 985-986 (1922). (3) Nieuwland, Vogt, Foohey, *J. Am. Chem. Soc.* 52, 1018-1024 (1930).

3:6215 2-CHLORO-4-METHYLPHENOL  $\text{C}_7\text{H}_7\text{OCl}$  Beil. VI - 492  
 (2-Chloro-*p*-cresol)



B.P. 195-196° at 760 mm. (2)  $D_4^{27} = 1.1785$  (10)  $n_D^{27} = 1.5200$  (10)  
 197-198° at 738 mm.  $D_{25}^{25} = 1.2196$  (1)  
 195-197° (10)

Clear odorless liq. with characteristic disagreeable persistent odor. — Slightly sol. aq.; sol. alc., ether,  $\text{C}_6\text{H}_6$ .

[For prepn. from 2-chloro-4-methylaniline via diazo reaction see (3); from sodium *p*-cresolate in  $\text{CS}_2$  see (1); from *p*-cresol with  $\text{Cl}_2$  in  $\text{CCl}_4$  (4) or with  $\text{SO}_2\text{Cl}_2$  (77% yield (10)) see indic. refs.]

$\bar{C}$  in 5 pts. AcOH and treated with 2 pts. conc.  $\text{HNO}_3$  ( $D = 1A$ ), or  $\bar{C}$  dislvd. in 10 pts.

AcOH and grad. treated with powd.  $\text{NaNO}_2$  (5), yields on pptn. with aq. 2-chloro-4-methyl-6-nitrophenol [Beil. VI-413], golden-yel. ndls. from dil. alc. or dil. AcOH, m.p.  $65^\circ$  (5). [Note that addition of  $\bar{C}$  to fuming  $\text{HNO}_3$  ( $D = 1.5$ ) leads to its oxidn. (evoln. of nitrous fumes), nitration, and wandering of methyl group (6).]

The methyl ether of  $\bar{C}$  [Beil. VI-403], 2-chloro-4-methylanisole, b.p.  $215-218^\circ$  cor. at 760 mm., has been prepd. only indirectly.

⑦ 2-Chloro-4-methylphenyl benzoate: pl. from pet. eth., m.p.  $71-72^\circ$  (7). [This benzoate htd. with 0.7 of its wt. of  $\text{AlCl}_3$  for 10 min. at  $140^\circ$  gives by Fries rearrangement 92% yield (8) of 2-hydroxy-3-chloro-5-methylbenzophenone, yel. lfts. from MeOH, m.p.  $71^\circ$  (8) cf. (9) ]

3:6215 (1) Schall, Dralle, *Ber.* 17, 2528-2529 (1884). (2) Klarmann, Shternov, Gates, *J. Am. Chem. Soc.* 55, 2585 (1933). (3) Cain, Norman, *J. Chem. Soc.* 89, 24 (1906). (4) Zincke, *Ann.* 328, 277 (1903). (5) Zincke, *Ann.* 328, 311-312 (1903). (6) Zincke, *Ann.* 328, 314 (1903). (7) von Auwers, *Ber.* 44, 801 (1911). (8) Rosenmund, Schnurr, *Ann.* 460, 86 (1928). (9) von Auwers, Mauss, *Ann.* 464, 310 (1928). (10) Sah, Anderson, *J. Am. Chem. Soc.* 63, 3165 (1941).

3:6220  $\beta, \gamma$ -DICHLORO- $n$ -PROPYL ACETATE  $\text{C}_5\text{H}_8\text{O}_2\text{Cl}_2$  Beil. II - 129  
(Glycerol  $\alpha, \beta$ -dichlorohydrin  $\Pi_1$ -(58)  
 $\alpha$ -acetate,  $\gamma$ -aceto- $\alpha, \beta$ -dichlorohydrin)  $\Pi_2$ -  

$$\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{HC}-\text{Cl} \\ | \\ \text{CH}_2\text{O.CO.CH}_3 \end{array}$$

B.P.  $107-108^\circ$  (1)  $D_4^{25} = 1.1672$  (3)  
 $101-102^\circ$  cor. at 755 mm. (2)  
 $115-120^\circ$  at 40 mm. (3) (4)  
 $89-91^\circ$  at 16 mm. (5)  
 $81-83^\circ$  at 12 mm. (2)

[For prepn. of  $\bar{C}$  from 2,3-dichloropropanol-1 (" $\beta$ -dichlorohydrin") (3:6060) with  $\text{Ac}_2\text{O}$  see (3); from glycerol  $\alpha, \alpha'$ -diacetate with  $\text{PCl}_5$  or  $\text{S}_2\text{Cl}_2$  see (2); from allyl chloride (3:7035) with acetyl hypochlorite see (6) ]

$\bar{C}$  on keeping decomposes, perhaps by hydrolysis (2). [For study of hydrolysis with  $N/10$   $\text{HCl}$  see (1).] —  $\bar{C}$  with MeOH + trace  $\text{HCl}$  gives by alcoholysis (5) (6) 2,3-dichloropropanol-1 (3:6060) + MeOAc

3:6220 (1) Bancroft, *J. Am. Chem. Soc.* 41, 425 (1919). (2) Wegscheider, Zmerzlikar, *Monatsh.* 34, 1074-1079 (1913). (3) de la Acona, *Compt rend* 139, 868 (1904). (4) Gibson, *J. Soc. Chem. Ind.* 50, 950 (1931). (5) Delaby, Dubois, *Bull. soc. chim.* (4) 47, 572 (1930). (6) Bockemüller, Hoffmann, *Ann.* 519, 189-190 (1935).

3:6230  $\beta$ -CHLOROETHYL CHLOROACETATE  $\text{C}_4\text{H}_8\text{O}_2\text{Cl}_2$  Beil. II - 198  
 $\text{ClCH}_2\text{CH}_2\text{O.CO.CH}_2\text{Cl}$   $\Pi_1$ -  
 $\Pi_2$ -

B.P.  $107-108^\circ$  (1)  $D_4^{25} = 1.317$  (1)  
 $04-05^\circ$  at 12 mm. (3)

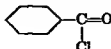
[For prepn. from ethylene chlorohydrin (3:5552) + chloroacetyl chloride (3:5235) see (1); for prepn. from ethylene oxide (1:6105) + chloroacetyl chloride see (3).]

$\bar{C}$  on boiling with aq. hydrolyzes to  $\beta$ -chloroethanol (3:5552) and chloroacetic ac. (3:1370).

3:6230 (1) Henry, *Bull. soc. chim.* (2) 42, 260 (1894). (2) Mulder, Bremer, *Ber.*, 11, 1960 (1878). (3) Altwegg, Landriven, U.S. 1,393,161, Oct. 11, 1921; *Cent.* 1922, IV 947.



## 3:6240 BENZOYL CHLORIDE

 $C_7H_5OCl$ Beil. IX - 182  
IX<sub>1</sub>-(94)

## B.P.

## M.P.

199°	at 760 mm. (1)	-0.5° (4)	$D_4^{25} = 1.2070$ (20)
	(25)	(22)	$n_D^{25} = 1.5520$ (9)
198.3°	at 749.4 mm. (1)	-0.6° (3)	1.5508 (20)
198-198.3 cor.	at 749.4 mm. (2)	-1.0° (1)	$D_4^{30.9} = 1.2105$ (24)
197.9°	(3)	(23)	$n_D^{30.9} = 1.55376$ (24)
197.3°	at 754 mm. (4)		$D_4^{20} = 1.2122$ (14)
197.21°	at 760 mm. (5)		1.2113 (4)
197.2°-197.3°	(6)		$n_D^{20} = 1.55369$ (14)
197.2° cor.	at 760 mm. (7)		1.55354 (3)
197.1-197.6°	(8)		1.5536 (4)
197°	(9)		$D_4^{15} = 1.2188$ (25)
196.8-197.0°	at 764 mm. (10)		$n_D^{15} = 1.55799$ (25)
196.2-196.5° cor.	at 751.3 mm. (11)		
196.8° cor.	at 746 mm. (12)		
194.5-196° cor.	at 746 mm. (13)		
193.9-194.1°	at 742.2 mm. (14)		
100.5° at 35.5 mm. (10)	83.47° at 16 mm. (5)	75° at 10.5 mm. (10)	
96.1° at 30 mm. (10)	82.5° at 15.5 mm. (10)	74° at 10 mm. (10)	
94.5° at 29 mm. (10)	82.10° at 15 mm. (5)	74.0-74.2° at 9.5 mm. (8)	
92.5° at 26 mm. (10)	80.59° at 14 mm. (5)	71° at 9 mm. (10)	
93° at 20 mm. (15)	79° at 13 mm. (10)	77.8-78.0° at 8 mm. (18)	
87.5° at 20 mm. (10)	82° at 12 mm. (15)	67.6-67.8° at 7.5 mm. (19)	
87° at 19.5 mm. (10)	78.8° at 10.5 mm. (17)	49-50° at 2.5-3.0 mm. (20)	

Note 1. For vapor press.  
of  $\bar{C}$  for range  $T = 85.4$ -  
105.5° see also (21).

MISCELLANEOUS PHYSICAL PROPERTIES OF  $\bar{C}$ BINARY SYSTEMS CONTAINING  $\bar{C}$ 

$\bar{C}$  + inorganic compounds.  $\bar{C}$  +  $AlCl_3$ : m.p. 93° (22), 95° (26); for prepn. from  $\bar{C}$  +  $AlCl_3$  in  $CS_2$  see (26); for thermal anal. (eutectic with  $\bar{C}$  has m.p. -7.5° and conts. 87.3 wt. %  $\bar{C}$ ) see (22); for conductivity of  $AlCl_3$  in  $\bar{C}$  see (27); for study of mol. wt. in  $C_6H_6$  see (28).

$\bar{C}$  +  $AlBr_3$ : m.p. 90° (22); for thermal anal. (eutectic with  $\bar{C}$  has m.p. -5° and conts. 77.8 wt. %  $\bar{C}$  while eutectic with  $AlBr_3$  has m.p. abt. 7-8° and conts. 21 wt. %  $\bar{C}$ ) see (22); see also (30)

$\bar{C}$  +  $FeCl_3$ : scarlet red hygroscopic ndls. (31); for conductivity see (28).

$\bar{C}$  +  $SbCl_3$ : for thermal anal. (eutectic with  $\bar{C}$  has m.p. -23° and conts. 55 wt. %  $\bar{C}$ ) see (32).

$\bar{C}$  +  $SbCl_5$ : for prepn. see (34); for conductivity in liq.  $SO_2$  see (33).

$\bar{C}$  +  $SbBr_3$ : for thermal anal. (eutectic with  $\bar{C}$  has m.p. -6° and conts. 68 wt. %  $\bar{C}$ ) see (32).

$\bar{C}$  + organic compounds.  $\bar{C}$  +  $C_6H_6$ : for thermal anal. (eutectic has m.p.  $-26.8^\circ$  and conts. 63.6 wt. %  $\bar{C}$ ) see (35). —  $\bar{C}$  + *p*-xylene: for thermal anal. (eutectic has m.p.  $-18.5^\circ$  and conts. 67.2 wt. %  $\bar{C}$ ) see (35). —  $\bar{C}$  + *mesitylene*: for thermal anal. (eutectic has m.p.  $-70^\circ$  and conts. abt. 20 wt. %  $\bar{C}$ ) see (35). —  $\bar{C}$  + *biphenyl*: for thermal anal. (eutectic has m.p.  $-8^\circ$  and conts. 81.8 wt. %  $\bar{C}$ ) see (35). —  $\bar{C}$  + *diphenylmethane*: for thermal anal. (eutectic has m.p.  $-15^\circ$  and conts. 66.7 wt. %  $\bar{C}$ ) see (35).

$\bar{C}$  + *chlorobenzene*: for thermal anal. (eutectic has m.p.  $-54.2^\circ$  and conts. 19.3 wt. %  $\bar{C}$ ) see (35). —  $\bar{C}$  + *nitrobenzene*: for thermal anal. (eutectic has m.p.  $-20.5^\circ$  and conts. 50 wt. %  $\bar{C}$ ) see (35).

## PREPARATION OF $\bar{C}$

Note that comml.  $\bar{C}$  is often contaminated with various chlorobenzoyl chlorides (e.g., *o*-chlorobenzoyl chloride (3:6640), *m*-chlorobenzoyl chloride (3:6590), *p*-chlorobenzoyl chloride (3:6550), etc.), with traces of benzaldehyde (1:0195), or with benzoic acid (1:0715) + HCl from hydrolysis. For removal of BzOH + HCl from  $\bar{C}$  by shaking its  $C_6H_6$  soln. with cold aq. 5%  $NaHCO_3$  see (12); by treatment with metallic oxides or carbonates see (36).

From benzoic acid. [For prepn. of  $\bar{C}$  from benzoic acid (1:0715) with  $PCl_5$  (70% yield (37)) (10) (38), with  $PCl_3$  (39) (40) in pres. of  $ZnCl_2$  (77% yield (37)) or in pres. of a little aq. at  $100^\circ$  under press (41), with  $SOCl_2$  (90% yield (37)) (42), with  $SCl_2$  in  $CS_2$  (43), with  $SiCl_4$  directly (23% yield (44)) or in  $C_6H_6$  (77% yield (44)), with  $POCl_3$  + alkali chloride at elev. temp. (45), or with dry HCl +  $P_2O_5$  at  $200^\circ$  (46) see indic. refs.]

[For prepn. of  $\bar{C}$  from benzoic acid (1:0715) with NaCl + Na or K pyrosulfate at  $200^\circ$  (47), or with Na chlorosulfonate (48) cf. (49), see indic. refs.]

[For prepn. of  $\bar{C}$  from benzoic acid (1:0715) with other organic acyl chlorides such as carbonyl chloride (phosgene) (3:5000) at  $140$ – $200^\circ$  (50) or in pres. of tertiary bases (such as pyridine) or their salts (51), with oxalyl (di)chloride (3:5060) (98% yield (15)), with *p*-toluenesulfonyl chloride in pyridine (52), or with  $\alpha,\beta$ -dichloroethyl ethyl ether (3:5640) (53). see indic. refs.]

From salts of benzoic acid. Note that with salts of benzoic acid more or less formn. of benzoic anhydride (1:0595) may occur.

[For prepn. of  $\bar{C}$  from NaOBz with  $POCl_3$  (2) (54), with  $SCl_2$  at room temp. (55) cf. (43), with  $SO_2$  +  $Cl_2$  (56), with Na chlorosulfonate (48) cf. (49), or with benzenesulfonyl chloride (57) see indic. refs.]

[For prepn. of  $\bar{C}$  from AgOBz with carbonyl chloride (3:5000) in s.t. at  $100^\circ$  see (58).]

From dibenzoyl peroxide. [For prepn. of  $\bar{C}$  from dibenzoyl peroxide (1:4930) with oxalyl (di)chloride (3:5060) refluxed in dark for 24 hrs. (70% yield (59)), with  $PCl_5$  in pet. ether (60), with  $AlCl_3$  in  $CHCl_3$  at  $0^\circ$  (61) or in  $C_6H_6$  at  $100^\circ$  (62), or with  $FeCl_3$  in  $C_6H_6$  at  $100^\circ$  (62) see indic. refs.]

From other benzoic acid derivatives. [For formn. of  $\bar{C}$  from benzamide with dry HCl or AcCl at  $140^\circ$  see (63); from methyl benzoate (1:3586) with  $PCl_5$  at  $160$ – $180^\circ$  (64) or from ethyl benzoate (1:3721) with  $PCl_5$  in s.t. at  $140^\circ$  (65) see indic. refs.; from  $\alpha,\beta$ -dichloroethyl benzoate or from  $\alpha$ -chloroethyl benzoate on htg. in pres. of traces of  $ZnCl_2$  see (66); from benzoic anhydride (1:0595) with  $PCl_5$  +  $Cl_2$  (67) or with carbonyl chloride (3:5000) (68) see indic. refs.]

From benzaldehyde. [For formn. of  $\bar{C}$  from benzaldehyde (1:0195) with  $SO_2Cl_2$  (5 moles) on distn. (69), with  $S_2Cl_2$  in s.t. at  $150^\circ$  (107), with  $POCl_3$  in  $C_6H_6$  (70), with NOCl (71), with EtOCl (3:7022) (72), with *ter*-AmOCl (3:9237) (8.5% soln. in  $CCl_4$ ) at room temp. for 15 hrs. (73), or with  $Cl_2$  (91) (105) (106) see indic. refs.]

From henzotrichloride. [For prepn. of  $\bar{C}$  from benzotrichloride (3:6540) by partial hydrolysis with limited amt. of aq. in pres. of  $H_2SO_4$  or  $FeCl_3$  (74), with aq. vapor over tin phosphate at  $240^\circ$  (75), with ord. comml.  $ZnCl_2$  at  $120^\circ$  (76) in pres. of limited aq. (77) (note that pure  $ZnCl_2$  fails to react but addn. of 1 mole aq. or initial use of tech.  $ZnCl_2$  gives  $\bar{C}$  (76)), with pure  $ZnO$  at  $100^\circ$  (76), with  $BzOH$  in boilg. nitrobenzene (78) or in pres. of  $ZnCl_2$  (80), with  $NH_4OBz$  at  $200-210^\circ$  as directed (79), or with  $EtOH$  in pres. of  $FeCl_3$  or  $Fe$  (81) see indic. refs.]

Note that benzotrichloride (3:6540) on heating with carboxylic acids or anhydrides, especially in pres. of  $ZnCl_2$ , is often employed to prepare a mixture of  $\bar{C}$  with the acid chloride corresponding to the acid or anhydride so employed, particularly in cases where the two acyl chlorides are readily separable. [E.g., note that henzotrichloride (3:6540) with phthalic anhydride (1:0725) (81) (82) or phthalic acid (1:0820) (83) +  $ZnCl_2$  at  $110-120^\circ$  gives (96% yield (82))  $\bar{C}$  + (93% yield (82)) *sym.*-phthalyl (di)chloride (3:6900); benzotrichloride with  $AcOH$  (1:1010) in pres. of an acid cat. gives (84) (85) (86) (87)  $\bar{C}$  + acetyl chloride (3:7065); for other examples see under chloroacetyl chloride (3:5235), dichloroacetyl chloride (3:5290), trichloroacetyl chloride (3:5420), fumaryl (di)chloride (3:5875), and terephthalyl (di)chloride (3:2205). Similarly, henzotrichloride (3:6540) with salts of sulfonic acids yields  $\bar{C}$  + the corresp. arylsulfonyl chlorides; e.g., benzotrichloride with sodium  $\beta$ -naphthalenesulfonate gives (88) 90% yield  $\bar{C}$  + 80% yield  $\beta$ -naphthalenesulfonyl chloride.]

From henzal (di)chloride. [For formn. of  $\bar{C}$  from henzal (di)chloride (3:6327) with  $O_2$  in u.v. light (89), with air in pres. of  $Ni$  at  $160^\circ$  (90), or with  $BzOH$  (1:0715) +  $Cl_2$  at  $125-175^\circ$  (91) see indic. refs.]

From miscellaneous sources. [For formn. of  $\bar{C}$  from benzyl alc. (1:6480) with  $Cl_2$  (92) or with  $SOCl_2$  at  $180^\circ$  (103), from benzyl acetate (1:3751) with  $Cl_2$  at  $150-170^\circ$  (104), from thiohenzoyl chloride +  $O_2$  at  $100-120^\circ$  (93), from henzonitrile with  $NOCl$  at  $180^\circ$  (94), from tolan (diphenylacetylene) with  $NOCl$  at  $150-200^\circ$  (95), from dihenzoyltartaric anhydride +  $PCl_5$  (3 moles) in s.t. at  $130^\circ$  for 3 hrs. (note that chlorofumaryl dichloride is also formed) (96), from *N,N*-dibenzoylaniline (dibenzanilide) with dry  $HCl$  at  $250-270^\circ$  (note that henzanilide is also formed) (97), from  $\alpha$ -chloro- $\alpha$ -nitro-phenylacetamide on dry htg. (98), from phthalic anhydride (1:0725) +  $HCl$  gas +  $CrCl_3$  or  $ZnCl_2$  at  $290-300^\circ$  under press. (99), or from  $C_6H_6$  (1:7400) with carbonyl chloride (phosgene) (3:5000) +  $AlCl_3$  (100) (101), or with oxalyl (di)chloride (3:5060) +  $AlCl_3$  (102) see indic. refs.]

### CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis. [ $\bar{C}$  in  $N_2$  through porcelain tube at  $550-600^\circ$  (108) or over  $Ni$  at  $420^\circ$  (109) cf. (110) gives  $CO$ , chlorobenzene (3:7903), and other products;  $\bar{C}$  over finely divided  $Cu$  at  $420-450^\circ$  gives (110) benzoic anhydride (1:0595) +  $HCl$ ;  $\bar{C}$  over  $BaCl_2$  at  $420-450^\circ$  gives (110) benzoic anhydride (1:0595) and other products. For study of effect of radium radiation at  $2-12^\circ$  over 7-8 month period see (13).]

Reduction. [ $\bar{C}$  with  $H_2$  in boilg. xylene in pres. of  $PtO_2$  + trace of thiourea (111),  $Pd/BaSO_4$  (112), or powd.  $Ni$  (112), or  $\bar{C}$  over  $Pd$  at  $200-230^\circ$  (113) cf. (114) gives (yields: 96% (111), 87-89% (113)) benzaldehyde (1:0195); for study of purification of xylene as solvent for cat. reduction of  $\bar{C}$  see (115); for study of influence of various other solvents see (116) (112).]

[ $\bar{C}$  with  $H_2$  in pres. of  $NiCl_2$  at  $270-280^\circ$  gives (110) benzene, toluene, biphenyl +  $HCl$ ;  $\bar{C}$  with copper hydride is claimed (117) to yield benzaldehyde but this could not be confirmed (118).  $\bar{C}$  with chromous acetate in 50%  $KOH$  gives (very small yield (119)), benzyl alc. (1:6480), while  $\bar{C}$  with  $LiH$  in high-boilg. pet. ether at  $130^\circ$  gives (presumably by subsequent condensation of the intermediate benzaldehyde) 65% yield (120) benzyl benzoate (1:4422).]

[ $\bar{C}$  with Na/Hg + stream of dry HCl gives (121) benzyl alc. (1:6480);  $\bar{C}$  with Na/Hg in dry ether gives (122) (123) (124) benzyl alc. (1:6480), benzoic acid (1:0715), benzil (1:9015),  $\alpha, \alpha'$ -dibenzoxystilbene ("isobenzil") [Beil. IX-138], and  $\alpha, \alpha'$ -dibenzoxydibenzyl [Beil. IX-136];  $\bar{C}$  with Na in moist ether gives (125) benzyl alc. (1:6480), benzoic acid (1:0715), and benzyl benzoate (1:4422).]

Oxidation. [ $\bar{C}$  on oxidn. in pres. of hydrocarbon peroxides and various oxidn. cat. is claimed (126) to give dibenzoyl peroxide (1:4930); see also below under behavior of  $\bar{C}$  with  $\text{Na}_2\text{O}_2$ .]

Chlorination. [ $\bar{C}$  on monochlorination with  $\text{Cl}_2$  nt  $35^\circ$  in pres. of  $\text{FeCl}_3$  gives (10) cf. (127) mainly a mixt. of chlorobenzoyl chlorides (83.5% *m*- (3:6590) + 14.5% *o*- (3:6640) + 2.0% *p*- (3:6550)) accompanied by a small amt. of dichlorobenzoyl chlorides; for extensive study of effect of using higher proportion of  $\text{Cl}_2$  under otherwise same conditions see (128). Note, however, that  $\bar{C}$  with 3 moles  $\text{Cl}_2$  in s. t. gives (129) (130) a mixt. of addn. products, such as 1,2,3,4,5,6-hexachlorohexahydrobenzoyl chloride, substitution products, and materials formed by both addition and substitution (130).]

Sulfonation. [ $\bar{C}$  cannot be sulfonated without accompanying hydrolysis of the acyl chloride function (131) (132) (133) (134) (137), the end prod. of these sulfonation processes is, therefore, not *m*-sulfobenzoyl chloride (apparently still unknown cf. (135)) but rather *m*-sulfobenzoic acid [Beil. XI-384, XI<sub>1</sub>-(98)]. However,  $\bar{C}$  added to conc.  $\text{H}_2\text{SO}_4$  at  $0-40^\circ$  gives (136) a cryst. addn. prod.  $\bar{C} \cdot \text{H}_2\text{SO}_4$  which on stdg. loses HCl forming benzoyl hydrogen sulfate [Beil. IX<sub>1</sub>-(94)] but shows no transformation into *m*-sulfobenzoic acid even after 6 months over dry alkali even though HCl is lost completely (136). At  $100^\circ$  conversion of benzoyl hydrogen sulfate occurred very slowly and the prod. consisted of *o*-sulfobenzoic acid (not *meta*) (136).]

## BEHAVIOR OF $\bar{C}$ WITH OTHER INORGANIC REAGENTS

$\bar{C}$  with HF. [ $\bar{C}$  with HF as directed (138) (139) or with dry  $\text{KHF}_2$  in Cu retort (140) (141) (142), with  $\text{ZnF}_2$  nt  $195^\circ$  (11) (143), with  $\text{AgF}$  in s. t. at  $190^\circ$  for 6 hrs. (144), or with 3 moles  $\text{SbF}_3$  (145) gives (yields: 67-80% (140), 76% (145), 69% (11)) benzoyl fluoride, b.p.  $161.5^\circ$  at 745 mm. (142),  $159^\circ$  (139),  $156^\circ$  (146),  $155-156^\circ$  at 760 mm. (11),  $155^\circ$  (138),  $154-155^\circ$  (143),  $151^\circ$  u. c. at 736 mm. (141),  $145^\circ$  (144). Note, however, that  $\bar{C}$  with KF in anhydrous formic acid gives (147) formyl fluoride, b.p.  $26^\circ$  at 750 mm. (147), while  $\bar{C}$  with KF in AcOH gives (147) acetyl fluoride, b.p.  $20-22^\circ$  (147).]

$\bar{C}$  with HBr. [ $\bar{C}$  with dry HBr gas at  $100^\circ$  gives (148) benzoyl bromide [Beil. IX-195, IX<sub>1</sub>-(95)], b.p.  $218-219^\circ$  cor. at 760 mm. (149),  $215.0^\circ$  at 741 mm. (150),  $90-91^\circ$  at 12 mm. (16), m.p.  $+8.1^\circ$  (150),  $D_4^{20} = 1.5461$  (150),  $n_D^{20} = 1.5900$  (150).]

$\bar{C}$  with HI. [ $\bar{C}$  with excess HI at ord. temp. (148) (16), or  $\bar{C}$  with Mg +  $\text{I}_2$  in dry ether (151), gives benzoyl iodide [Beil. IX-195, IX<sub>1</sub>-(95)], b.p.  $109-109.5^\circ$  at 10 mm. (148) cf. (16). Note that  $\bar{C}$  with KI does not (152) give benzoyl iodide.]

$\bar{C}$  with metals. [ $\bar{C}$  with Na in dry ether stood 10 days at room temp. gives (86% yield (153)) (154) ethyl benzoate (1:3721) but  $\bar{C}$  with Na/Hg in dry ether causes the reaction to take a more complicated course (see above under reduction of  $\bar{C}$ ).  $\bar{C}$  with Na vapor gives (155) cf. (154) benzil (1:9015).  $\bar{C}$  with K in xylene refluxed 2 days gives (153) benzoic anhydride (1.0595).]

[For behavior of  $\bar{C}$  with Zn in dry ether or in di-isoamyl ether at  $20-32^\circ$  see (156). For behavior of  $\bar{C}$  with finely divided Cu or Ni at elevated temps. see above under pyrolysis of  $\bar{C}$ .]

## $\bar{C}$ WITH VARIOUS METAL OXIDES OR SALTS

$\bar{C}$  with  $\text{Na}_2\text{O}_2$ . [ $\bar{C}$  with  $\text{Na}_2\text{O}_2$  in water at  $5^\circ$  (157) cf. (159) or  $\bar{C}$  with 30%  $\text{H}_2\text{O}_2$  + aq. NaOH (158) cf. (159) gives (yields: 91% (157), 60-70% (158)) benzoyl hydrogen peroxide

(perbenzoic acid) [Beil. IX-178, IX-1(93)], m.p. 42°. For other methods for prepn. of perbenzoic acid such as from dibenzoyl peroxide with  $\text{NaOCH}_3$  in  $\text{MeOH}/\text{CHCl}_3$  (160) or with  $\text{NaOC}_2\text{H}_5$  in  $\text{EtOH}/\text{toluene}$  (161), or from benzaldehyde in acetone with air (162), see indic. refs. For study of Na perbenzoate (157) and its use in purification (163) of perbenzoic acid see indic. refs.]

[ $\text{C}$  with  $\text{Na}_2\text{O}_2$  in aq. at 0° (164) (165) or in aq. acetone (166), or  $\text{C}$  with aq.  $\text{H}_2\text{O}_2$  +  $\text{NaOH}$  (167) or aq.  $\text{H}_2\text{O}_2$  + iron-free  $\text{Ca}(\text{OH})_2$  (168), or  $\text{C}$  with aq.  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$  (169) (170) (171), or  $\text{C}$  with perbenzoic acid (see preceding paragraph) + aq.  $\text{NaHCO}_3$  (172) gives dibenzoyl peroxide [Beil. IX-170, IX-1(93)], m.p. 105°. For review of prepn. and properties of this prod. see also (173).]

$\text{C}$  with misc. salts.  $\text{C}$  on warming with various inorganic salts yields benzoic anhydride. [E.g.,  $\text{C}$  with  $\text{NaNO}_2$  (174) cf. (175) (176), with  $\text{KNO}_3$  (177), with  $\text{Pb}(\text{NO}_3)_2$  (178), with nitrates of other heavy metals (179), with  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  in aq. soln. at 60° (180), with  $\text{K}_2\text{S}_2\text{O}_8$  in pyridine (181), with  $\text{Na}_2\text{SO}_3$  in pyridine (183) in pres. of  $\text{C}_6\text{H}_6$  (181) cf. (182), or with  $\text{BaO}$  at 140–150° (184) gives benzoic anhydride (1:0595), m.p. 42°. For other methods of conversion of  $\text{C}$  to benzoic anhydride see above under pyrolysis of  $\text{C}$  and below under behavior of  $\text{C}$  with organic acids and their salts.]

$\text{C}$  with  $\text{NaN}_3$ . [ $\text{C}$  with  $\text{NaN}_3$  in aq. acetone at 0° (185), or in dry ether (186), gives (54.6% yield (185)) benzoyl azide (benzazido) [Beil. IX-332], m.p. 32° (185). Note that although this prod. readily explodes on htg. (187) (188) yet in inert solvents such as  $\text{C}_6\text{H}_6$  (194) it smoothly decomposes into  $\text{N}_2$  and phenyl isocyanate (for study of mechanism see (189)); under certain circumstances the latter may be hydrolytically split to aniline cf. (190). For studies on decomposition of benzoyl azide by ultrasonic waves see (185) (193).]

### HYDROLYSIS OF $\text{C}$

$\text{C}$  with cold aq. is slowly and with warm aq. rapidly hydrolyzed (195) to benzoic acid (1:9716) and  $\text{HCl}$ . [For study of rate of hydrolysis of  $\text{C}$  in ether with aq. at 20–22° (195) or at 0° (148), in 50% aq. acetone at 0° in pres. of  $\text{H}_2\text{SO}_4$  (196) cf. (198), in various other organic solvents immiscible with aq. (197) or with  $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$  at 158° (199) see indic. refs.]

$\text{C}$  with aq. alkali on warming readily yields (195) alkali benzoate + alkali chloride. Note that  $\text{C}$  in 50% aq. pyridine hydrolyzes much faster than in aq.  $\text{NaOH}$  or aq.  $\text{Na}_2\text{CO}_3$  (39) (use in determination of atomic weight of carbon by hydrolysis of  $\text{C}$  and pptn. of  $\text{AgCl}$  (39)). Note that rate of hydrolysis of  $\text{C}$  is 2000 times as fast (200) as that of benzyl chloride (3:8535).

[Note that  $\text{C}$  in  $\text{Ac}_2\text{O}$  soln. behaves as an acid (201) and can be titrated (202) with  $\text{NaOAc}$  in  $\text{Ac}_2\text{O}$ .]

### BEHAVIOR OF $\text{C}$ WITH VARIOUS INORGANIC SULFUR COMPOUNDS

With  $\text{H}_2\text{S}$ . [The behavior of  $\text{C}$  with  $\text{H}_2\text{S}$  is disputed; on one hand  $\text{C}$  in dry pyridine treated with  $\text{H}_2\text{S}$  at 5° and subsequently acidified is claimed (203) to give thiolbenzoic acid,  $\text{C}_6\text{H}_5\text{CO}_2\text{SH}$  [Beil. IX-419, IX-1(169)] (see next paragraph); on the other hand  $\text{C}$  refluxed in dry pyridine in stream of  $\text{H}_2\text{S}$  is claimed (204) to yield thiolbenzoic acid ( $\text{C}_6\text{H}_5\text{CS})_2\text{O}$ , colorless cryst. from hot alc.]

With $\text{KSH}$ . [ $\text{C}$ with cold alc. $\text{KSH}$ (207) (209) (8) salt of thiolbenzoic acid (207) (208), b.p. 98.0–98.6° at II–12 that this product is readily by air or mild oxidizing agent air followed by $\text{H}_2\text{O}_2$ as di	KOH with $\text{H}_2\text{S}$ (IX-419, 0.05 mm. (8) dibenzoyl dis (35% aq. 5–10° (211)
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in acetone followed by  $I_2/KI$  oxidn. (213), or with  $HSMgBr$  followed by air oxidn. (208) gives (65-70% yield (210)) dibenzoyl disulfide [Beil. IX-424], cryst. from 1,2-dichloroethane (3:5130) (210) (211) (212), m.p. 128-129° (210) (211) (212); this prod. has considerable pharmaceutical interest as an antipruritic; for hydrolysis to benzoic acid as method of detn. see (210) (214).]

#### BEHAVIOR OF $\bar{C}$ WITH VARIOUS INORGANIC NITROGEN COMPOUNDS

With  $NH_3$ . [ $\bar{C}$  with conc. aq.  $NH_4OH$  (215), with dry  $NH_3$  (105), with liq.  $NH_3$  (216), with solid  $(NH_4)_2CO_3$  (217), or with  $KNH_2$  in dry ether (218) gives benzamide [Beil. IX-195, IX<sub>1</sub>-(96)], m.p. 130°; note that either the  $(NH_4)_2CO_3$  (219) or  $KNH_2$  (218) methods may give also small amounts of *N*-benzoylbenzamide (dibenzamide) [Beil. IX-213, IX<sub>1</sub>-(104)], m.p. 148°, and/or *N,N*-dibenzoylbenzamide (tribenzamide) [Beil. IX-214, IX<sub>1</sub>-(104)], m.p. 207-208°. However,  $\bar{C}$  with  $NH_3$  gas over  $Al_2O_3$  at 490-500° gives (220) benzonitrile [Beil. IX-275, IX<sub>1</sub>-(121)], b.p. 191°, m.p. -13°.]

With  $NH_2OH$ . [ $\bar{C}$  in  $C_6H_6$  with free  $NH_2OH$  (221), or  $\bar{C}$  in  $C_6H_6$  with  $NH_2OH.HCl$  + pyridine (221), or  $\bar{C}$  in ether with  $NH_2OH.HCl$  +  $Na_2CO_3$  (221), gives benzohydroxamic acid (*N*-benzoylhydroxylamine) [Beil. IX-301, IX<sub>1</sub>-(128)], cryst. from  $EtOAc$ , m.p. 128°. Note that  $\bar{C}$  with aq.  $NH_2OH$  solns. (222) also gives side reactions which diminish yield and increase difficulty of purification of prod.; also that  $\bar{C}$  with  $NH_2OH.HCl$  in toluene gives (222) benzohydroxamic acid benzoate (dibenzohydroxamic acid) [Beil. IX-303, IX<sub>1</sub>-(128)] and other products. For alternative method of prepn. of benzohydroxamic acid from ethyl benzoate (1:3721) with  $NH_2OH.HCl$  +  $MeOH/KOH$  see (223); for review of utility of hydroxamic acids in org. qual. anal. see (224); for study of formn. of benzohydroxamic acid and its  $FeCl_3$  color reaction as method of detn. of hydroxylamine see (230).]

With  $NH_2NH_2$ . [ $\bar{C}$  (1 mole) with  $N_2H_4.H_2O$  (2 moles) in ether gives (225) benzhydrazide (*N*-benzoylhydrazine) [Beil. IX-319, IX<sub>1</sub>-(129)], m.p. 112°, but this prod. is usually better obtd. from reaction of  $N_2H_4.H_2O$  with  $MeOBz$  (1:3586) (226) or  $EtOBz$  (1:3721) (227) (228).  $\bar{C}$  (1 mole) with  $N_2H_4.H_2SO_4$  (0.5 mole) + aq.  $NaOH$  (2.3 moles) as directed gives (66-75% yield (228)) *N,N'*-dibenzoylhydrazine [Beil. IX-324, IX<sub>1</sub>-(131)], ndls. from  $AcOH$  (228) or  $EtOH$  (229), m.p. 237-238° (229).]

#### BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

##### BEHAVIOR OF $\bar{C}$ WITH HYDROCARBONS

With cycloalkanes. [ $\bar{C}$  with cyclohexane (1:8405) +  $AlCl_3$  gives (19% yield (231)) phenyl 2-methylcyclopentyl ketone, b.p. 160-162° at 36 mm.,  $D_4^{18} = 1.0255$ ,  $n_D^{18} = 1.5380$ , accompanied by much benzaldehyde (1:0195) presumably formed from  $\bar{C}$  by the hydrogen corresp. to coupling of 2 moles of cyclohexane.]

With alkenes. [ $\bar{C}$  with ethylene +  $AlCl_3$  in special apparatus as directed gives (87-92% yield (232)) phenyl  $\beta$ -chloroethyl ketone ( $\beta$ -chloropropiophenone) (3:1115); cf. also (233).]

With cycloalkenes. [ $\bar{C}$  with cyclohexene (1:8070) +  $AlCl_3$  in  $CS_2$  gives by addition phenyl 2-chlorocyclohexyl ketone (234), which on dehydrochlorination in the pres. of  $AlCl_3$  (234) or with alc.  $KOH$  (235) gives (40% yield (235)) phenyl cyclohexenyl ketone (tetrahydrobenzophenone), b.p. 147° at 8 mm.,  $D_4^{22} = 1.070$ ,  $n_D^{22} = 1.5595$  (235).]

With alkynes. [For behavior of  $\bar{C}$  with heptyne-1 (1:8085) in pres. of  $AlCl_3$ ,  $ZnCl_2$ ,  $SnCl_4$ ,  $BF_3$ , etc., see (236).]

With aromatic hydrocarbons. [ $\bar{C}$  with  $C_6H_6$  in pres. of  $AlCl_3$  gives (yields: 74% (237), 71-74% (238)) (210) (241) (242) (243) (244) (245) benzophenone (1:5150), but best (239) prepn. of latter is from  $C_6H_6$  +  $CCl_4$  (3:5100) +  $AlCl_3$ . — For studies of substitution for

$\text{AlCl}_3$  of  $\text{FeCl}_3$  {237} {238} {246} {247} {248},  $\text{FeCl}_3 + \text{AlCl}_3$  {249},  $\text{GaCl}_3$  {250},  $\text{TiCl}_3$  {251},  $\text{WCl}_6$  {252},  $\text{UCl}_4$  {252},  $\text{ZrCl}_4$  {253}, Cr powder {254},  $\text{ZnCl}_2$  {238},  $\text{SbCl}_3$  {255} {256}, or  $\text{SbBr}_3$  {257} see indic. refs. —  $\bar{\text{C}}$  with  $\text{C}_6\text{H}_6$  in liq.  $\text{HCl}$  at 200° and 250 pounds press. {258} or in pres. of  $\text{P}_2\text{O}_5$  in s.t. at 180–200° {259} {260} gives small yield of benzophenone (1:5150). —  $\bar{\text{C}}$  with  $\text{C}_6\text{D}_6 + \text{AlCl}_3$  in  $\text{CS}_2$  gives {261} phenyl pentadeuterophenyl ketone, b.p. 160° at 15 mm. (corresp. oxime, m.p. 140°, does not depress m.p. of ordinary benzophenone oxime.)]

[ $\bar{\text{C}}$  with toluene in pres. of  $\text{AlCl}_3$  gives {262} {263} {264} mainly phenyl *p*-tolyl ketone (1:5160) together with some phenyl *o*-tolyl ketone [Beil. VII-439, VII<sub>1</sub>-(234)]. For studies of substitution for  $\text{AlCl}_3$  of  $\text{FeCl}_3$  {263},  $\text{FeCl}_3 + \text{AlCl}_3$  {265}, or  $\text{SbCl}_3$  {255} {256} see indic. refs.]

[For reaction of  $\bar{\text{C}}$  in pres. of  $\text{AlCl}_3$  with *o*-xylene (1:7430) {262}, *m*-xylene (1:7420) {262} {266} {267}, *p*-xylene (1:7415) {262}, ethylbenzene {268} {266} {269}, see indic. refs.]

[ $\bar{\text{C}}$  with biphenyl (1:7175) in pres. of  $\text{AlCl}_3$  gives (yields: 75% {270}, 60% {271}) {272} {273} {274} {275} {276} {242} phenyl *p*-xenyl ketone (*p*-phenylbenzophenone) [Beil. VII-521, VII<sub>1</sub>-(290)], scales from alc., m.p. 106° cor. {270}, 106° {272} {273}, 102–103° {275}, 102° {271} {274}, 101–102° {242}, 101° {276}; b.p. 413° at 758 mm. {271}, 419–420° at 744 mm. {274}, 258° at 10 mm. {276} (corresp. oxime exists in two stereoisomeric forms {277}, m.p. 200° and 173°, usual mixt. having m.p. 193–194° {278}, 186–187° {271}; corresp. 2,4-dinitrophenylhydrazones, m.p. 217–217.5° {271}); for use of  $\text{P}_2\text{O}_5$  (instead of  $\text{AlCl}_3$ ) in prepn. of *p*-phenylbenzophenone (above) see {279}. Note that the isomeric *o*-phenylbenzophenone, m.p. 86–87°, has been prepared indirectly {280}.]

[ $\bar{\text{C}}$  with naphthalene (1:7200) in pres. of  $\text{AlCl}_3$  in  $\text{CS}_2$  {281} {282} {283} {284} {285} {286} or without solvent at 150° {286}, or in liq.  $\text{SO}_2$  {287}, or  $\bar{\text{C}}$  with naphthalene in pres. of  $\text{ZnCl}_2$  at 125° {280} cf. {288} {289} or of  $\text{P}_2\text{O}_5$  {289} {279} {259} {260}, gives (yields: 85% {282}, 52% {287}) mainly phenyl  $\alpha$ -naphthyl ketone (1-benzoylnaphthalene) [Beil. VII-510, VII<sub>1</sub>-(283)], pr. from alc., m.p. 75.5–76° {276}, 75.5° {282}, 75–70° {281}, 75° {283}, b.p. 336° at 764 mm. {284}, 222° at 8 mm. {276}; note that this prod. is usually accompanied by some phenyl  $\beta$ -naphthyl ketone (2-benzoylnaphthalene) [Beil. VII-511, VII<sub>1</sub>-(283)], ndls. from alc., m.p. 82° {276} {289}, 81–83° {281}, b.p. 398° at 754 mm. {284}, 225° at 8 mm. {276}.]

[For reaction of  $\bar{\text{C}}$  with anthracene (1:7285) +  $\text{AlCl}_3$  in  $\text{CS}_2$  {277} {290} {291} {292} {293}, or in nitrobenzene at –10° {294}, or without  $\text{AlCl}_3$  in boiling nitrobenzene {295} giving (yields: 85% {277}, 78% {290}) 9-benzoylanthracene ( $\alpha$ -anthraphenone) [Beil. VII-538], cryst. from  $\text{EtOAc}$ , m.p. 145.5–146° {277}, see indic. refs.; note, however, that for prepn. of this prod. use of benzoic anhydride (1:0595) (rather than  $\bar{\text{C}}$ ) is preferred {296}. — For reaction of  $\bar{\text{C}}$  with phenanthrene (1:7240) +  $\text{AlCl}_3$  in  $\text{CS}_2$  {297} {298} or in nitrobenzene {298} see indic. refs.]

With heterocyclic parent nuclei. The behavior of  $\bar{\text{C}}$  with furan (1:8015) in the pres. of Friedel-Crafts cat. has apparently not been reported [however, the prod. to be expected, viz., phenyl  $\alpha$ -furyl ketone [Beil. XVII-348, XVII<sub>1</sub>-(186)], b.p. 285° at 759 mm. {299}, 186° at 46 mm. {299}, 164° at 19 mm. {299},  $D_{20}^{20} = 1.1732$  {300},  $D_{10}^{10} = 1.1839$  {299},  $n_D^{20} = 1.6055$  {299}, 1.5798 {300}, has been obt'd. (49% yield {301}) from benzoic anhydride (1:0595) with furan (1:8015) +  $\text{SnCl}_4$  in  $\text{C}_6\text{H}_6$ , and from furoyl chloride (3:8515) with  $\text{C}_6\text{H}_6$  in pres. of  $\text{AlCl}_3$  {299}.]

[ $\bar{\text{C}}$  with thiophene in pres. of  $\text{AlCl}_3$  {302},  $\text{SnCl}_4$  {303} {304},  $\text{P}_2\text{O}_5$  {305}, or  $\alpha$ -thienylmercuric chloride {306} cf. {307} {308} gives (yields: 89–90% {302}, 82.5% {304}) phenyl  $\alpha$ -thienyl ketone [Beil. XV11-348, XVII<sub>1</sub>-(187)], m.p. 56° {305} {307}, 55.5–56° {306}, 55–56° {302}, 55° {303} {304}.]

BEHAVIOR OF  $\bar{C}$  WITH ORGANIC HYDROXYL COMPOUNDS

$\bar{C}$  with organic OH or SH compounds (or their metallic salts) gives in general the corresponding benzoates. With phenols, however, there is also the additional possibility (according to the conditions employed) of either direct nuclear benzylation or Fries rearrangement of the benzoate esters to give phenolic ketones.

Esterification of alcohols or phenols with  $\bar{C}$  in presence of aqueous alkali comprises a general procedure first discovered by Lossen (309) and later developed and extended by Schotten, Baumann, and others. The reaction is not restricted to the use of benzoyl chloride but covers acid halides in general, e.g., acetyl chloride, *p*-nitrobenzoyl chloride, 3,5-dinitrobenzoyl chloride, benzenesulfonyl chloride, etc.

For detailed quantitative study of the influence of conditions on the Schotten-Baumann reaction see (310); for study of its application to *p*-nitrobenzoyl chloride (311) or of 3,5-dinitrobenzoyl chloride (312) in the derivatization of alcohols in dilute aqueous solution see indic. refs.; for study of substitution of the acyl halide by the corresponding anhydride see (313).

Note that in general the yield of ester is improved by use of low temperature ( $0^\circ$ - $25^\circ$ ) (310), by use of relatively concentrated solutions of both the hydroxyl compound and the alkali (310), and sometimes by additions of NaOAc or other salts. (311).

With monohydric alcohols.  $\bar{C}$  with monohydric alcs. gives the corresponding alkyl benzoates.

[E.g.,  $\bar{C}$  with MeOH (1:6120) gives methyl benzoate (1:3586), b.p.  $199.6^\circ$ , m.p.  $-12.5^\circ$  (for study of rate of reaction at  $0^\circ$  and  $25^\circ$  see (18)). —  $\bar{C}$  with EtOH (1:6130) gives ethyl benzoate (1:3721), b.p.  $213.2^\circ$ , m.p.  $-34.2^\circ$  (for study of rate of esterification at  $0^\circ$  (17) or at  $25^\circ$  in various solvents (314) see indic. refs. —  $\bar{C}$  with *n*-PrOH (1:6150) gives *n*-propyl benzoate (3:3917), b.p.  $231^\circ$ . —  $\bar{C}$  with isopropyl alc. (1:6135) gives isopropyl benzoate (1:3766), b.p.  $218.5^\circ$  (for study of rate of esterification at  $25^\circ$  (6) or at  $30^\circ$  (11) (315) see indic. refs.)]

$\bar{C}$  with *n*-BuOH (1:6180) gives *n*-butyl benzoate (1:4104), b.p.  $250.3^\circ$ , m.p.  $-22.4^\circ$ . —  $\bar{C}$  with isobutyl alc. (1:6165) gives isobutyl benzoate (1:4006), b.p.  $242.2^\circ$  cor. —  $\bar{C}$  with *sec*-BuOH (1:6155) gives (yields 75% (316), 66% (317), 20% (318)) *sec*-butyl benzoate [Beil. IX-112, IX<sub>1</sub>-(63)], b.p.  $234.5$ - $235.5^\circ$  cor. at 757 mm. (317),  $148$ - $151^\circ$  at 50 mm. (317),  $115$ - $117^\circ$  at  $20^\circ$  (319),  $112$ - $116^\circ$  at 14 mm (318),  $D_4^{25} = 0.9945$  (317),  $n_D^{25} = 1.4933$  (319). —  $\bar{C}$  with *ter*-BuOH (1:6140) in pres. of pyridine gives (yields 86% (320), 80% (321) (322)) *ter*-butyl benzoate [Beil. IX<sub>1</sub>-(64)], b.p.  $112^\circ$  at 18 mm. (321),  $91$ - $92^\circ$  at 8 mm. (323),  $91.3^\circ$  at 7.5 mm. (320),  $96^\circ$  at 2 mm. (322);  $D_4^{25} = 0.9928$  (322);  $n_D^{25} = 1.4896$  (322) (321),  $n_D^{20} = 1.4910$  (320).]

$\bar{C}$  with *n*-AmOH (1:6205) gives *n*-amyl benzoate [Beil. IX<sub>1</sub>-(64)], b.p.  $138$ - $139^\circ$  at 15 mm (316),  $137$ - $138^\circ$  at 15 mm. (324). —  $\bar{C}$  with isoamyl alc. (1:6200) gives isoamyl benzoate (1:4166), b.p.  $262.3^\circ$  cor. at 760 mm. —  $\bar{C}$  with neopentyl alc. (1:5812) gives (325) neopentyl benzoate, b.p.  $235$ - $237^\circ$  at 740 mm.,  $110$ - $111^\circ$  at 10 mm.,  $D_4^{25} = 0.9817$ ,  $n_D^{25} = 1.4875$  (325).]

$\bar{C}$  reacts with other alcohols and thiols similarly, but details cannot be tabulated here.

With phenols.  $\bar{C}$  can react with phenols in either or both of two modes; on one hand it can benzyolate the phenolic OH yielding the corresponding phenol benzoates (a list of the melting points of 88 phenols of Order 1 is given on page 635 of Vol. I of this series (326); for study of effect of structure on rate of benzyolation of various monohydric phenols see (329)); on the other hand  $\bar{C}$  may under certain conditions effect the direct nuclear benzyolation of phenols. Since the phenolic ketones thus formed may also be more or less readily obtained by catalyzed rearrangement of the phenol benzoates, the chemistry of the phenol



benzoates and their rearrangement products is so voluminous that it cannot here be given detailed discussion. [For extensive reviews of the Fries rearrangement (327) (328) of phenol esters (including the benzoates) see indie. refs.]

With enols (or their metallic derivatives). With methyl acetoacetate.  $\bar{C}$  with the Na enolate of methyl acetoacetate (1:1705) gives (330) methyl  $\alpha$ -benzoylacetate, b.p. 136–137° at 2 mm. (corresp. Cu enolate, blue-green ndls. from dioxane, m.p. 226–228°; corresp. semicarbazone, prepd. by indirect means, m.p. 166° (331)).]

With ethyl acetoacetate.  $\bar{C}$  with the Na enolate of ethyl acetoacetate (1:1710) gives (yields: 74.8% (332), 67% (333), 63–75% (334) cf. (335) (337) ethyl  $\alpha$ -benzoylacetate [Beil. X-817, X<sub>1</sub>-(396)], b.p. 202° at 50 mm. (335), 177–181° at 20 mm. (334), 175–176° sl. dec. at 12 mm. (337), 169° sl. dec. at 11 mm. (338), 165–167° at 10 mm. (333) (corresp. Cu enolate, m.p. 224° (336), 221–222° (339)). Note that this prod. upon cleavage of the acetyl group, e.g., with aq.  $NH_4OH + NH_4Cl$ , gives (77–78% yield (334)) (332) ethyl benzoylacetate (1:1778), for alternative prepn. of which see (340). — Note, however, that two forms of the isomeric ethyl *O*-benzoylacetate are known (341); a liq. form, b.p. 153–155° at 3 mm., prepd. from ethyl acetoacetate (1:1710) with  $\bar{C} +$  pyridine, and a solid form, m.p. 42°, prepd. from the Cu enolate of ethyl acetoacetate (1:1710) with  $\bar{C}$  in ether (for much further detail see (341)).]

With acetylacetone.  $\bar{C}$  with the Na enolate (342) or K enolate (343) of acetylacetone (1:1700) in ether gives (50% yield (343)) *O*-benzoylacetylacetone ( $\alpha$ -benzoyl- $\alpha$ -acetylacetone) [Beil. VII-865, VII<sub>1</sub>-(474)], m.p. 35° (342), 34–35° (343), b.p. 167° at 22 mm. (342), accompanied by some of the higher-melting form, m.p. 103° (342), 102–103° (343), of its benzoate [Beil. IX-150]; note that the lower-melting form, m.p. 66–67° (344), is obt'd. from  $\alpha$ -benzoyl- $\alpha$ -acetylacetone (above) with  $\bar{C}$  in pyridine (344).]

With benzoylacetone.  $\bar{C}$  with Na enolate of benzoylacetone (1:1450) under various conditions gives (345) (346) (347) cf. (348)  $\alpha,\alpha$ -dibenzoylacetone [Beil. VII-872, VII<sub>1</sub>-(480)] (q.v. for constants of various enol and keto forms) and/or the corresp. benzoate [Beil. IX-157], m.p. 87–88° (349).]

With dibenzoylmethane.  $\bar{C}$  with Na enolate of dibenzoylmethane (1:1480) gives (45% yield (350)) (351) (352) (353) tribenzoylmethane [Beil. VII-877, VII<sub>1</sub>-(485)] (q.v. for constants of various forms) and/or the corresp. benzoate [Beil. IX-158], m.p. 121–122° (351).]

#### BEHAVIOR OF $\bar{C}$ WITH ETHERS

With aliphatic ethers. Acyl chlorides with aliphatic ethers do not react even at elevated temperatures (354) although acid bromides (e.g., acetyl bromide (355)) or acyl iodides (e.g., benzoyl iodide (356)) are able to effect cleavage into alkyl halides and alkyl esters. However, when acyl chlorides are heated with aliphatic ethers in the presence of certain metallic salts, cleavage of the ethers is more or less readily effected. Although the topic cannot here be pursued exhaustively, several examples are cited in the following text.

$\bar{C}$  with diethyl ether (1:6110) on hgt. in pres. of  $ZnCl_2$  (354) (357) (358) (359) (360),  $SnCl_4$  (358),  $ZrCl_4$  (358),  $TiCl_4$  (358) (362),  $SbCl_5$  (358),  $FeCl_3$  (358) (301),  $AlCl_3$  (358) (362), or  $SbCl_3$  (358) gives ethyl benzoate (1:3721); note, however, that use of  $BF_3$ ,  $CuCl_2$ , and  $SnCl_2$  gives only traces while  $SiCl_4$ ,  $PCl_5$ ,  $PCl_3$ ,  $BCl_3$ ,  $AsCl_3$ , or  $MgCl_2$  achieves no cleavage (358) of the ether. Note that by extension of the  $ZnCl_2$  method to use of 3,5-dinitrobenzoyl chloride a procedure for the identifi. of ethers as the corresp. alkyl 3,5-dinitrobenzoates has been described (363) cf. (364).]

With phenol ethers. With phenol ethers where no phenolic OH remains to interfere,  $\bar{C}$  reacts in the pres. of suitable cat. in the Friedel-Crafts sense. Although the topic cannot here be pursued exhaustively, several examples are cited in the following text.

[ $\bar{C}$  with methyl phenyl ether (anisole) (1:7445) +  $AlCl_3$  in  $CS_2$  solution (81% yield (365)) (366) (367) cf. (368) (360) or without other solvent (369) gives mainly *p*-anisyl phenyl ketone (*p*-methoxybenzophenone) (1:5170), m.p. 62° (366) (367) (370), 61–62° (365) (369), 61° (371), h.p. 354–355° at 729 mm. (371); this prod. is accompanied by some *o*-anisyl phenyl ketone (*o*-methoxybenzophenone) (1:5142), m.p. 39°, which is separable from the main prod. only by repeated recrystallization from lgr. (b.p. 40–60°) and alc. (369).]

[ $\bar{C}$  with ethyl phenyl ether (phenetole) (1:7485) +  $AlCl_3$  in  $CS_2$  soln. (yields: 83% (372), 73% (374) (369) (366) (373) or without other solvent (369) gives mainly *p*-phenetyl phenyl ketone (*p*-ethoxybenzophenone) [Beil. VIII-159, VIII<sub>1</sub>-(569)], m.p. 47–48° (374), 47° (369) (372), 46.5° (373), 38–39° (366), b.p. 245–250° at 25 mm. (374), 227° at 21 mm. (373), 215–225° at 15 mm. (373) (corresp. oxime, m.p. 135–136° (374)), accompanied by some *o*-phenetyl phenyl ketone (*o*-ethoxybenzophenone) which (although not further characterized) is liq. and readily separable.]

[ $\bar{C}$  with diphenyl ether (1:7125) +  $AlCl_3$  in  $CS_2$  (375) (376) (374), or  $\bar{C}$  with diphenyl ether (1:7125) +  $HgCl_2$  at 150–160° (377) (27% yield), or  $\bar{C}$  with phenyl 4-chloromercuriphenyl ether at 150° (377), gives (yields: 97% (375), 95% (374), 70% (377)) *p*-phenoxybenzophenone [Beil. VIII-159], m.p. 71° cor. (375), 70–71° (374), 66° (377) (corresp. oxime, m.p. 124° (374)); for further benzoylation of this prod. to *bis*-(*p*-benzoylphenyl) ether, m.p. 163–164°, see (376).]

[ $\bar{C}$  with methyl  $\alpha$ -naphthyl ether (1:7630) +  $AlCl_3$  in  $CS_2$  (378) or in nitrobenzene (379) gives (84% yield (379)) 4-benzoyl-1-methoxynaphthalene, m.p. 82–83° (378), 81–82° (379); for high-press. hydrogenation of this prod. giving (84–86% yield) 4-benzyl-1-methoxynaphthalene, m.p. 83–84°, see (379). —  $\bar{C}$  with methyl  $\beta$ -naphthyl ether (1:7180) +  $AlCl_3$  in  $CS_2$  gives (85% yield (380)) 1-benzoyl-2-methoxynaphthalene, m.p. 125° cor.; note that use of 1,1,2,2-tetrachloroethane as solvent is much less satisfactory (381). —  $\bar{C}$  with ethyl  $\alpha$ -naphthyl ether (1:7635) +  $AlCl_3$  in  $CS_2$  gives (386) (382) 4-benzoyl-1-ethoxynaphthalene [Beil. VIII-207, VIII<sub>1</sub>-(586)], m.p. 74–75° (386), accompanied (383) by some 4-benzoylnaphthol-1 and other products. — The presumably analogous reaction of  $\bar{C}$  with ethyl  $\beta$ -naphthyl ether (1:7135) +  $AlCl_3$  appears not to have been studied, and the expected 1-benzoyl-2-ethoxynaphthalene is unreported.]

#### BEHAVIOR OF $\bar{C}$ WITH ACIDS (OR THEIR SALTS)

With sodium formate. [ $\bar{C}$  with  $NaOOCH$  on htg. (384) gives  $BzOH$  (1:0715),  $CO$ , +  $HCl$ .]

With acetic acid. [ $\bar{C}$  with  $AcOH$  (1:1010) refluxed in pres. of charcoal (385), or in pres. of a tertiary base (386) even at ord. temp., or  $\bar{C}$  with  $NaOAc$  on warming (387) cf. (388) (389) gives the mixed anhydride,  $CH_3CO.O.CO.C_6H_5$  [Beil. IX-163], accompanied by various other products. Note, however, that  $\bar{C}$  with  $AcOH$  (1:1010) at 100° for 3 hrs. gives (70% yield (147)) acetyl chloride (3:7065) while  $\bar{C}$  with  $Ac_2O$  (1:1015) at 100° for 1 hr. gives (77% yield (147)) acetyl chloride (3:7065) accompanied by benzoic anhydride (1:0595). For prepn. of acetic-benzoic anhydride by other means, e.g., from benzoic acid (1:0715) with ketene (390), and for study of its use in Friedel-Crafts type reactions (391), see indic. refs.]

With benzoic acid. [ $\bar{C}$  with benzoic acid (1:0715) in s.t. at 160–200° for 12 hrs. (392), or at 220° under reduced press. (397), or with pyridine (389) (393), or  $\bar{C}$  with  $NaOBz$  shaken with aq. (394) or htd. at 130° (395), gives benzoic anhydride (1:0595), m.p. 42°, h.p. 360°; for other modes of formn. of this prod. from  $\bar{C}$  see above under behavior of  $\bar{C}$  with various inorganic salts; for prepn. (72–74% yield) of benzoic anhydride (1:0595) from benzoic acid (1:0715) by use of acetic anhydride (1:1015) see (396).]



With aromatic secondary amines.  $\bar{C}$  with aromatic secondary amines gives the corresponding *N*-benzoyl derivatives but note that these same products are frequently also obtained by reaction of  $\bar{C}$  with the appropriate tertiary amines.

[ $\bar{C}$  with *N*-methylaniline (437), or  $\bar{C}$  with *N,N*-dimethylaniline at 190° (438), gives *N*-benzoyl-*N*-methylaniline (*N*-methylbenzanilide) [Beil. XII-260], scales from lgr., m.p. 63° (438), 59° (437), b.p. 331-332° (439) —  $\bar{C}$  with *N*-ethylaniline (not actually reported) or  $\bar{C}$  with *N,N*-diethylaniline at 200° (438) gives *N*-benzoyl-*N*-ethylaniline (*N*-ethylbenzanilide) [Beil. XII-270], cryst. from ether + lgr., m.p. 54° (440), 52° (441), 60° (438).]

[ $\bar{C}$  with *N*-methyl- $\alpha$ -toluidine should yield *N*-benzoyl-*N*-methyl- $\alpha$ -toluidine (*N*-methylbenzo- $\alpha$ -toluidide) [Beil. XII-796], pr. from ether/lgr., m.p. 65-66°, and  $\bar{C}$  with *N*-ethyl- $\alpha$ -toluidine should yield *N*-benzoyl-*N*-ethyl- $\alpha$ -toluidine (*N*-ethylbenzo- $\alpha$ -toluidide) [Beil. XII-796], pr. from ether/lgr., m.p. 71-72°, but both these products have been reported only by indirect means (442) — The analogous products to be expected from  $\bar{C}$  with *N*-methyl (or *N*-ethyl)-*m*-toluidine, or  $\bar{C}$  with *N*-methyl (or *N*-ethyl)-*p*-toluidine, have not been characterized in the literature.]

[ $\bar{C}$  with *N*-methyl- $\alpha$ -naphthylamine should yield *N*-benzoyl-*N*-methyl- $\alpha$ -naphthylamine [Beil. XII-1234], cryst. from  $C_6H_6$ /lgr., m.p. 121°, but this prod. has actually been reported only from  $\bar{C}$  with *N,N*-dimethyl- $\alpha$ -naphthylamine at 170-190° (438). — Similarly,  $\bar{C}$  with *N*-methyl- $\beta$ -naphthylamine + aq alk yields (443) *N*-benzoyl-*N*-methyl- $\beta$ -naphthylamine [Beil. XII-1287, XII<sub>1</sub>- (539)], ndls from pet. eth., m.p. 84° (443); this prod. is also claimed (438) from *N,N*-dimethyl- $\beta$ -naphthylamine at 170-180° but the m.p. of 169° is not in accord with the later work under mild conditions and presumably represents an isomeric material. — The analogous benzoyl derivatives of *N*-ethyl- $\alpha$ -naphthylamine and of *N*-ethyl- $\beta$ -naphthylamine are unreported.]

[ $\bar{C}$  with diphenylamine on warming (444) in ether soln. (445) gives *N*-benzoyldiphenylamine (*N,N*-diphenylbenzamide) [Beil. XII-270, XII<sub>1</sub>- (201)], cryst. from alc., m.p. 180° (435), 179-180° (446), 177° (447).]

$\bar{C}$  with heterocyclic secondary amines.  $\bar{C}$  with piperidine [Beil. XX-6, XX<sub>1</sub>- (5)] directly (536) or better in aq. NaOH (537) (538) (539) gives (87-91% yield (537)) *N*-benzoyl-piperidine [Beil. XX-46, XX<sub>1</sub>- (15)], m.p. 49° (540), 48° (538), 44° (537); b.p. 320-321° (541), 240-244° at 130 mm. (537), 193° at 25 mm (541), 180-184° at 20 mm (537), 172-174° at 12 mm. (537); not volatile with steam (538). [Note that this prod. with  $PBr_3$  (542) (543) (544) (545) (546), with  $PBr_3 + Br_2$  (547), or with  $PCl_3 + Br_2$  (548) comprises an important method of preparation of pentamethylene dibromide (1,5-dibromopentane).]

$\bar{C}$  with morpholine [Beil. XXVII-5] in ether gives (549) *N*-benzoylmorpholine, ens. sol. aq., pr. from dry ether, m.p. 74-75° (549).

$\bar{C}$  with aromatic diamines. [ $\bar{C}$  with *o*-phenylenediamine [Beil. XIII-6, XIII<sub>1</sub>- (5)] in aq. NaOH (448), or  $\bar{C}$  with *o*-phenylenediamine hydrochloride in aq. soln. (449), gives *N,N'*-dibenzoyl-*o*-phenylenediamine [Beil. XIII-21, XIII<sub>1</sub>- (8)], ndls. from AcOH, m.p. 301° (450), about 300° dec. (451) — Note that this prod. on htg. above m.p. (450), or on htg. with conc. HCl in s.t. at 200° (449), gives 2-phenylbenzimidazole [Beil. XXIII-230, XXIII<sub>1</sub>- (61)], m.p. variously reported around 290°, which latter, although stable toward  $\bar{C}$  at 260° (452), yet with  $\bar{C}$  + aq. NaOH in cold (450) reverts to *N,N'*-dibenzoyl-*o*-phenylenediamine (above). — Note that *N*-benzoyl-*o*-phenylenediamine [Beil. XIII-20, XIII<sub>1</sub>- (8)], m.p. 140° (453), has been reported only by indirect means (453) (454); on htg. 2 hrs. at 140° followed by a few minutes at 280° (455) it gives 2-phenylbenzimidazole (see above). — Note finally that 1-benzoylbenzimidazole [Beil. XXIII-133, XXIII<sub>1</sub>- (35)], m.p. 93-94° (456), 91-92° (450), on htg. with  $\bar{C}$  (457), or benzimidazole itself with  $\bar{C}$  + aq. NaOH (450), both give *N,N'*-dibenzoyl-*o*-phenylenediamine (above).]

[ $\bar{C}$  with hydrochloride of *m*-phenylenediamine [Beil. XIII-33, XIII<sub>1</sub>- (10)] on htg. gives

(458) *N,N'*-dibenzoyl-*m*-phenylenediamine [Beil. XIII-46], ndls. from AcOH, m.p. 240° (458) (460); for behavior of this prod. with  $\text{PCl}_5$  see (459). — Note that *N*-benzoyl-*m*-pbeoylenediamine (benz-*m*-aminoanilide) [Beil. XIII-46], m.p. 125°, has been reported only by indirect means (461) (462) (464).]

[ $\bar{\text{C}}$  with *p*-phenylenediamine [Beil. XIII-61, XIII<sub>1</sub>-(18)] + aq. NaOH (448) cf. (463) gives *N,N'*-dibenzoyl-*p*-pbenyleodiamine [Beil. XIII-98], m.p. above 300° (448) cf. (460); for behavior of this prod. with  $\text{PCl}_5$  see (459). — Note that *N*-benzoyl-*p*-pbenyleodiamine (benz-*p*-aminoanilide) [Beil. XIII-98, XIII<sub>1</sub>-(31)], m.p. 128° (452) (464), has been reported only by indirect means (452) (464).]

$\bar{\text{C}}$  with aminopheols.  $\bar{\text{C}}$  with *o*-aminophenol [Beil. XIII-354, XIII<sub>1</sub>-(103)] gives according to circumstances one of the two possible monobenzoyl derivatives, viz., *o*-(benzoylamino)phenol [Beil. XIII-372, XIII<sub>1</sub>-(115)] (or its ring-closure product, 2-phenylbenzoxazole-1,3 [Beil. XXVII-72, XXVII<sub>1</sub>-(235)]), or the dibenzoyl derivative, viz., *o*-benzoylamino-phenyl benzoate [Beil. XIII-373], as more fully described below. Note, however, that the other monobenzoyl derivative of *o*-aminophenol, viz., *O*-benzoyl-*o*-aminophenol or *o*-aminophenyl benzoate, known only as its hydrochloride, m.p. 149° (465), has been prepared only by indirect means (465) viz., from *O,N*-(dibenzoyl)-*o*-aminophenol, and on heating, or even on recrystn., loses HCl giving (465) 2-phenylbenzoxazole-1,3.

[ $\bar{\text{C}}$  (1 mole) with *o*-aminophenol (2 moles) in dry ether (466) gives *o*-(benzoylamino)phenol (*N*-benzoyl-*o*-aminophenol), tbs. from MeOH (465), lts. from  $\text{C}_6\text{H}_6$ , m.p. 169-171° u.c. (405), 169° (467), 167° (468) (corresp. acetate, m.p. abt. 140° (469) cf. (470); corresp. benzoate, m.p. 182° (470) (also below); corresp. benzenesulfonate, m.p. 90.5-91.0 (471)). — Note that this prod. on htg. above m.p. loses  $\text{H}_2\text{O}$  with ring closure yielding (468) 2-phenylbenzoxazole-1,3, m.p. 103° (see below). — Note also that *o*-(benzoylamino)phenyl benzoate (above) with  $\bar{\text{C}}$  in nitrobenzene refluxed 12 hrs. gives (479) *o*-(dibenzoylamino)phenyl benzoate, m.p. 170.5-171.5° (479).]

[ $\bar{\text{C}}$  with *o*-aminophenol on warming, followed by distn. of reaction product (472), or  $\bar{\text{C}}$  with *o*-aminophenol hydrochloride (468) (473) gives 2-phenylbenzoxazole-1,3, ads. from dil. alc., lts. from dil. HCl or dil.  $\text{H}_2\text{SO}_4$ , m.p. 103° (468) (472) (473) (474), volatile with steam, b.p. 314-317° (472) (corresp.  $\bar{\text{B}}$ .PhOH, m.p. 104° (477), corresp. MeI quaternary salt, m.p. 196° dec. (478).]

[ $\bar{\text{C}}$  (2 pts.) with *o*-aminophenol in aq. NaOH (448) or in pyridine +  $\text{CHCl}_3$  (465), or  $\bar{\text{C}}$  with *o*-aminophenol hydrochloride in  $\text{C}_6\text{H}_6$  at 100° (468), or  $\bar{\text{C}}$  + aq. NaOH with *o*-formylaminophenol (480), *o*-(acetylamino)phenol (481), or *o*-(benzoylamino)phenol (467), gives *O,N*-dibenzoyl-*o*-aminophenol (*o*-benzoylamino-phenyl benzoate), ndls. from alc. (480) or EtOAc (465), m.p. 185° (467), 183-184.5° (480), 182-183° (482), 181-182° (476), 180° (481), 179° u.c. (465). — Note that this prod. on boilg. with aq.  $\text{BaCO}_3$  (468) or for 2 days with alc. HCl (483) hydrolyzes at the ester linkage giving *o*-(benzoylamino)phenol, m.p. 169° (above).]

[ $\bar{\text{C}}$  with *m*-aminophenol [Beil. XIII-401, XIII<sub>1</sub>-(128)] in pyridine + ether (484) cf. (485) gives *m*-(benzoylamino)phenol [Beil. XIII-416], ndls. from toluene, m.p. 174° (485) (486), 173° (484). — Note that the isomeric *O*-benzoyl-*m*-aminophenol (*m*-aminophenyl benzoate) is unreported. —  $\bar{\text{C}}$  with *m*-aminophenol in aq. NaOH gives (486) *O,N*-dibenzoyl-*m*-aminophenol (*m*-(benzoylamino)phenyl benzoate) [Beil. XIII-416], pr. from  $\text{C}_6\text{H}_6$  or scales from abs. alc., m.p. 153° (486); this product with boilg. alc. KOH splits at the ester linkage giving (486) *m*-(benzoylamino)phenol (above), m.p. 174°.]

[ $\bar{\text{C}}$  with *p*-aminophenol [Beil. XIII-427, XIII<sub>1</sub>-(143)] in aq. NaOH (487), in pyridine (488), in alc. (489), or in ether + aq. NaOH (490) gives *p*-(benzoylamino)phenol (*N*-benzoyl-*p*-aminophenol) [Beil. XIII-469, XIII<sub>1</sub>-(165)], cryst. from AcOH, m.p. 216-217° (487), 214-215° (489) (for review of earlier confusion see (487)). — Note that the isomeric *O*-

benzoyl-*p*-aminophenol (*p*-aminophenyl benzoate) [Beil. XIII-440], m.p. 153–154° (491) (492), 148° (465), has been reported only by indirect means. —  $\bar{C}$  with *p*-aminophenol on htg. (472), or in aq. NaOH (448) (487) (488) or in pyridine (488), or  $\bar{C}$  with *p*-aminophenol hydrochloride (489) gives *O,N*-dibenzoyl-*p*-aminophenol (*p*-(benzoylamino)phenyl benzoate) [Beil. XIII-470, XIII<sub>1</sub>-(165)], cryst. from MeOH, EtOH, AcOH, or xylene, m.p. 235° (487) (467), 233–234° (489), 231° (472).]

The acylation of aminophenols (especially of the ortho series) and the relationships of the various multiple and mixed neyl derivatives have been extensively studied by Raiford (493)–(511), incl., Nelson (512)–(517), incl., and Bell (518) (519); the cited papers are arranged in chronological sequence for each worker.

$\bar{C}$  with tertiary amines.  $\bar{C}$  with certain tertiary amines especially in dry ether solution (520) forms addition products; these are presumably quaternary ammonium salts but have been very inadequately studied cf. (524).

[ $\bar{C}$  with  $Me_3N$  in ether at 0° or in  $C_6H_6$  at 80° fails to react (525). —  $\bar{C}$  with  $Et_3N$  in dry ether gives an immediate ppt. which increases on stdg. but appears to be a mixture of the expected addn. prod.,  $\bar{C} \cdot Et_3N$ , with triethylamine hydrochloride (520). —  $\bar{C}$  with triethylamine in dry ether after stdg. 2 months yields (520) long needles, m.p. 117°, whose analysis is in accord with "nearly pure" addn. prod.,  $\bar{C} \cdot (C_2H_5)_3N$ .]

[ $\bar{C}$  with *N,N*-dimethylaniline in dry ether in sunlight gives gradually hygroscopic crystals probably comprising the expected addn. prod.,  $\bar{C} \cdot C_6H_5N$ , (520). —  $\bar{C}$  with *N,N*-diethylaniline in dry ether gives (520) n crystals. prod. containing 71% of the expected  $\bar{C} \cdot C_{10}H_{15}N$ .]

[ $\bar{C}$  with pyridine in dry ether gives (520) a ppt. apparently contg. only 31% of the expected addn. prod.,  $\bar{C} \cdot C_5H_5N$ . —  $\bar{C}$  with pyridine in  $C_6H_6$  gives (521) pyridine hydrochloride, m.p. 144°. — For study of  $\bar{C}$  with pyridine in pres. of Zn dust giving the free radical *N*-benzoylpyridinium see (522); for study of  $\bar{C}$  with pyridine + *N,N*-dimethylaniline + Cu powder at 100° for 5 hrs. giving 4-(*p*-dimethylaminophenyl)pyridine see (523).]

Note that  $\bar{C}$  with pyridine in pres. of various inorganic salts gives benzoic anhydride; for further details see text above under behavior of  $\bar{C}$  with miscellaneous inorganic salts.

$\bar{C}$  with arylhydrazines.  $\bar{C}$  (1 mole) with phenylhydrazine (2 moles) [Beil. XV-67, XV<sub>1</sub>-(23)] in dry ether gives (526) *N'*-benzoyl-*N*-phenylhydrazine (also known as *sym*.-benzoyl-phenylhydrazine or  $\beta$ -benzoylphenylhydrazine) [Beil. XV-255, XV<sub>1</sub>-(67)], pr. from alc., m.p. 168° (526) (527). [Note that the isomeric *N*-benzoyl-*N*-phenylhydrazine (also known as *asym*.-benzoyl-phenylhydrazine or  $\alpha$ -benzoyl-phenylhydrazine) [Beil. XV-250, XV<sub>1</sub>-(65)], m.p. 70°, has been obtained only by indirect means, e.g., from  $\bar{C}$  with sodio-phenylhydrazine (528) or from *N*-chlorobenzaniline with  $NaNH_2$  (529). However,  $\bar{C}$  with phenylhydrazine hydrochloride in boilg.  $C_6H_6$  (530) (531), or  $\bar{C}$  with dry *K* phenylhydrazine- $\beta$ -sulfonate on htg. (526), or  $\bar{C}$  with  $\alpha$ -benzoyl-phenylhydrazine in ether (532), or  $\bar{C}$  with  $\beta$ -benzoyl-phenylhydrazine on htg. (526), gives *N,N'*-dibenzoyl-*N*-phenylhydrazine (also called  $\alpha,\beta$ -dibenzoyl-phenylhydrazine) [Beil. XV-261, XV<sub>1</sub>-(68)], pr. from alc., m.p. 177–178° (526) (530); note that this prod. on hydrolysis with alc. NaOH gives (533)  $\beta$ -benzoyl-phenylhydrazine (above).]

$\bar{C}$  with *p*-nitrophenylhydrazine [Beil. XV-468, XV<sub>1</sub>-(130)] presumably gives *N'*-benzoyl-*N*-(*p*-nitrophenyl)-hydrazine [Beil. XV-479, XV<sub>1</sub>-(140)], ndls. from alc., m.p. 193° (534), although this prod. is actually reported (534) only from benzoic anhydride (1:0595) with *p*-nitro-phenylhydrazine.

$\bar{C}$  with 2,4-dinitrophenylhydrazine [Beil. XV-489, XV<sub>1</sub>-(146)] in alc. suspension on warming gives (535) *N'*-benzoyl-*N*-(2,4-dinitrophenyl)-hydrazine [Beil. XV-492], or-red lfts. from alc., m.p. 206–207° (535).

$\bar{C}$  with diazomethane. [ $\bar{C}$  added slowly to excess  $CH_2N_2$  in ether at 0° gives (550) (551) (552) (553)  $\omega$ -diazoacetophenone [Beil. VII-362, XXIV-142]; this product may be caused

to undergo the Wolff rearrangement giving (554) phenylacetoacetic acid derivs. (e.g., amide or anilide (554)), or may be caused to react with HCl to give phenacyl chloride (3:1212); for comprehensive survey and review of the behavior of acyl halides with diazomethane see (555).]

$\bar{C}$  with miscellaneous nitrogen compounds. [For studies on the behavior of  $\bar{C}$  with indigo see (556) (557) (558) (559) (560) (561) (562) (563).]

#### BEHAVIOR OF $\bar{C}$ WITH ORGANOMETALLIC COMPOUNDS

Behavior of  $\bar{C}$  with Grignard reagents.  $\bar{C}$  with excess  $RMgX$  compounds in ether reacts in general to give the corresponding tertiary alcohols. Although extensive discussion of this reaction is manifestly infeasible here, the following examples are cited.

[ $\bar{C}$  with excess  $MeMgI$  gives (564) dimethyl-phenyl-carbinol [Beil. VI-506, VI<sub>2</sub>-(477)]. —  $\bar{C}$  with  $EtMgI$  gives (93% yield (565)) diethyl-phenyl-carbinol [Beil. VI-548, VI<sub>1</sub>-(269), VI<sub>2</sub>-(506)]. —  $\bar{C}$  with  $n\text{-}PrMgBr$  gives (81% yield (565)) di-*n*-propyl-phenyl-carbinol [Beil. VI<sub>1</sub>-(273), VI<sub>2</sub>-(513)]. —  $\bar{C}$  with  $C_6H_5MgBr$  as directed gives (91.5% yield (565)) triphenylcarbinol [Beil. VI-713, VI<sub>1</sub>-(349), VI<sub>2</sub>-(686)] (1:5935) accompanied by (7% yield (565)) biphenyl (1:7175); for study of limiting reaction of  $\bar{C}$  with  $C_6H_5MgBr$  to formation of diphenyl ketone (benzophenone) (1:5150) see (566); note also that  $\bar{C}$  with  $C_6H_5MgBr$  in presence of  $CoCl_2$  takes a different course yielding (567) benzoic acid, ethyl benzoate, biphenyl, benzophenone, phenylbenzoin, tetraphenylethylene oxide, and stilbene dibenzoate.]

[For interference of  $\bar{C}$  with the Gilman color test for  $RMgX$  compounds see (568).]

[For study of relative reactivity of  $\bar{C}$  as compared with various other organic compounds in competition for  $C_6H_5MgBr$  see (569) ]

Behavior of  $\bar{C}$  with other miscellaneous organometallic compounds. This topic cannot be treated extensively, but the following examples, mainly from the recent literature, will serve as lead references.

[ $\bar{C}$  with  $C_6H_5Li$  gives (570) no benzophenone and only 42% yield triphenylcarbinol (1:5985). —  $\bar{C}$  with  $Na$  phenylacetylene (571) (572) or  $Ag$  phenylacetylene (572) gives (74% yield (571)) phenyl phenylethynyl ketone (benzoyl-phenylacetylene) [Beil. VII-498, VII<sub>1</sub>-(275)].]

[ $\bar{C}$  +  $EtCu$  (573) in ether gives (22% yield (573)) ethyl phenyl ketone (propiophenone) (1:5525). —  $\bar{C}$  with  $C_6H_5Cu$  (573) in ether gives (55% yield (573)) benzophenone (1:5150).]

[ $\bar{C}$  +  $Et_2Hg$  gives (small yield (574)) propiophenone (1:5525). —  $\bar{C}$  with  $(C_6H_5)_2Hg$  in  $C_6H_6$  gives (575) benzophenone (1:5150). —  $\bar{C}$  with excess di-*p*-tolyl mercury in  $CCl_4$  fails (576) to react.]

[ $\bar{C}$  with  $Me_2Be$  gives (577) dimethyl-phenyl-carbinol [Beil. VI-506, VI<sub>2</sub>-(477)]. —  $\bar{C}$  with  $Me_2Cd$  gives (85% yield (578)) methyl phenyl ketone (acetophenone) (1:5515). —  $\bar{C}$  with  $Et_2Cd$  gives (50% yield (578)) ethyl phenyl ketone (propiophenone) (1:5525). —  $\bar{C}$  with  $(C_6H_5)_2Cd$  gives (57% yield (578)) diphenyl ketone (benzophenone) (1:5150). —  $\bar{C}$  with  $Me_2Zn$  gives (579) methyl phenyl ketone (acetophenone) (1:5515). —  $\bar{C}$  with  $Et_2Zn$  (580) (581) or with  $EtZnI$  (582) gives ethyl phenyl ketone (propiophenone) (1:5525).]

① Benzamide: cryst. from hot aq., m.p. 130°. [For methods of prepn. see above text under behavior of  $\bar{C}$  with various inorganic nitrogen compounds.]

② Benzanilide: lfts. from alc., m.p. 160°. [From  $\bar{C}$  with aniline directly (583), in ether contg. dry  $K_2CO_3$  (584), in  $C_6H_6$  (585), in toluene (586), in pyridine (or other tertiary amines) (587), in dil. aq. HCl (588), in  $AcOH/aq.$   $NaOAc$  (589), or aq.  $NaOH$ . — For study of rate of reaction of  $\bar{C}$  with aniline in aq. at various temperatures 0-60° (590),

in  $C_6H_6$  at  $25^\circ$  (591) cf. (585), in hexane at  $25^\circ$  (592), or in  $CCl_4$  at  $25^\circ$  (592) see indic. refs. — Note that  $\bar{C}$  with aniline hydrochloride in boilg.  $C_6H_6$  gives almost quant yield (530) benzanilide.]

① Benz-*o*-toluidide: ndls. from AcOEt/acetone, m.p.  $145-146^\circ$  (594) (595),  $144.3-144.6^\circ$  cor. (586),  $142-143^\circ$  (593),  $142^\circ$  (587). [From  $\bar{C}$  with *o*-toluidine (593) (594) in pres. of dil. (4%) aq. NaOH (595), or in pyridine (or other tertiary bases) (75% yield (587)), or in boilg. toluene (586).]

② Benz-*m*-toluidide: cryst. from dil alc, m.p.  $126^\circ$  (587),  $124.3-124.7^\circ$  cor. (586),  $125^\circ$  (596). [From  $\bar{C}$  with *m*-toluidine (596) in pyridine (or other tertiary bases) (80% yield (587)) or in boilg. toluene (586).]

③ Benz-*p*-toluidide: ndls. from alc., m.p.  $158^\circ$  (597),  $157.7-158.2^\circ$  cor. (586),  $157^\circ$  (587). [From  $\bar{C}$  with *p*-toluidine (598) (599) in pyridine (or other tertiary bases) (85% yield (587)) or in boilg. toluene (586).]

④ Benz- $\alpha$ -naphthalide: ndls. from alc. or AcOH, m.p.  $161-162^\circ$  (600),  $159-160^\circ$  (601) cor. (603),  $159^\circ$  (587),  $156^\circ$  (602),  $155-156^\circ$  (603). [From  $\bar{C}$  with  $\alpha$ -naphthylamine (604) (602) in aq. NaOH (603), pyridine (or other tertiary bases) (80% yield (587)), or in AcOH/aq. NaOAc (589). — For mol. cpd. of benz- $\alpha$ -naphthalide with 1,3,5-trinitrobenzene, viz.,  $\bar{C} \cdot C_6H_3(NO_2)_3$ , yel. ndls. from alc. soln. of components, m.p.  $131-132^\circ$  (605); see indic. refs. — For behavior of  $\bar{C}$  with  $\alpha$ -naphthylamine in pres. of  $ZnCl_2$  at  $175-180^\circ$  yielding 1-benzoylamino-4-benzoylnaphthalene, m.p.  $178^\circ$ , 1-benzoylamino-2,4-dibenzoylnaphthalene, m.p.  $224-226^\circ$ , etc., see (606) (607).]

⑤ Benz- $\beta$ -naphthalide: ndls. from  $C_6H_6$  or AcOH, m.p.  $162-163^\circ$  (609),  $162^\circ$  (587),  $161^\circ$  (612),  $157^\circ$  (610),  $156.5-157^\circ$  cor. (608). [From  $\bar{C}$  with  $\beta$ -naphthylamine (611) (610) in ether +  $K_2CO_3$  (612), in pyridine (or other tertiary bases) (80% yield (587)), or in AcOH/aq. NaOAc (589).]

⑥ Benzhydrazide: m.p.  $112^\circ$ . [See above text under behavior of  $\bar{C}$  with various inorganic nitrogen compounds, specifically with  $NH_2 \cdot NH_2$ .]

⑦  $\beta$ -Benzoylphenylhydrazine (*N*-Anilino benzhydrazide). pr. from alc., m.p.  $168^\circ$ . [See above text under behavior of  $\bar{C}$  with organic nitrogen compounds, specifically with arylhydrazines.]

⑧  $\beta$ -Benzoyl-*p*-nitrophenylhydrazine (*N*-(*p*-nitroanilino) benzhydrazide): ndls. from alc., m.p.  $193^\circ$ . See above text under behavior of  $\bar{C}$  with organic nitrogen compounds, specifically with arylhydrazines.

⑨  $\beta$ -Benzoyl-2,4-dinitrophenylhydrazine (*N*-(2,4-dinitroanilino) benzhydrazide): or-red lfts. from alc, m.p.  $206-207^\circ$ . [See above text under behavior of  $\bar{C}$  with organic nitrogen compounds, specifically with arylhydrazines.]

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## 3:6245 2,6-DICHLOROTOLUENE

 $C_7H_6Cl_2$ 

Beil V - 296

V<sub>1</sub>—  
V<sub>2</sub> (231)

B.P.

M.P.

200°	at 770 mm. (1)
199°	at 761 mm. (2)
198-200°	at 760 mm. (3)
197.7-198.1°	at 760 mm. (4)
196-198°	at 766 mm. (5)
194°	at 745 mm. (6)
82.5-82.8°	at 15 mm. (4)

5° (2) (3)  
4-5° (6) $D_{20}^{20} = 1.2535$  (6)



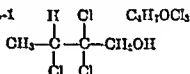


① 3-Chloro-4-methoxybenzenesulfonamide: cryst. from dil. alc., m.p. 130-131° u.c. (13), 130° cor. (14). [From  $\bar{C}$  + chlorosulfonic acid followed by conversion of the resultant sulfonyl chloride, m.p. 77-80° (14), to sulfonamide with  $(NH_4)_2CO_3$ ; 85% yield (13).] [A by-product, 3,3'-dichloro-1,4'-dimethoxydiphenyl sulfone, m.p. 165-166° cor. (14) (but unlike the sulfonamide insol. in alk.), has also been observed (14).]

3:6255 (1) Reitz, Ypsilanti, *Monatsh.* 66, 301 (1935). (2) Gattermann, *J. prakt. Chem.* (2) 59, 583 (1899). (3) Kohn, Sussmann, *Monatsh.* 49, 196-197 (1927). (4) Hayashi, *J. prakt. Chem.* (2) 123, 203 (1929). (5) Ingold, Smith, *J. Chem. Soc.* 1927, 1690-1695. (6) von Auwers, *Z. physik. Chem. A*-158, 418 (1932). (7) Holleman, *Rec. trav. chim.* 37, 104 (1918). (8) Fischli, *Ber.* 11, 1163 (1878). (9) Wallach, Heusler, *Ann.* 243, 237-238 (1888). (10) Meyer, *Monatsh.* 36, 726 (1915).

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— *d,l*-2,2,3-TRICHLOROBUTANOL-1



Beil. I - 369

I<sub>1</sub>—

I<sub>2</sub>-(398)

B.P. 199-200°

M.P. 62°

See 3:1336. Division A: Solids.

3:0270 2,6-DICHLOROTOLUENE



$C_7H_6Cl_2$

Beil. V - 296

V<sub>1</sub>—

V<sub>2</sub>-(231)

B.P.

199-200° at 760 mm. (13) (1)

196-200° (2)

108° at 760 mm. (3)

197-199° at 767 mm. (4)

54-56° at 8 mm. (5)

$D_4^{20} = 1.2686$  (5)

$n_D^{20} = 1.5510$  (5)

[For prepn. of  $\bar{C}$  from 6-chloro-2-aminotoluene (Beil. XII-836, XII-(389)) via diazotization and use of  $Cu_2Cl_2$  reactn. (70% yield (2)) (1) (3) see indic. refs.; from 2,6-dichlorotoluenesulfonic acid-4 (itself obtd. by chlorination of *p*-toluenesulfonyl chloride and subsequent hydrolysis) by hydrolysis in conc.  $H_2SO_4$  with superheated steam (yield 42-50% (5)) (4) (6) together with 2,3,6-trichlorotoluene (3:0625) as by-product (5) (6) see indic. refs.; for formn. of  $\bar{C}$  (together with other isomers) from toluene with  $Cl_2$  in pres. of  $MoCl_5$  (7) (8) (9), from *o*-chlorotoluene (3:8215) with  $Cl_2$  in pres. of Fe (9) or Al/Hg (10), or from 2,6-dichlorobenzaldehyde hydrazone by Wolff-Kishner reduction (32-36% yield (19)) see indic. refs.]

[ $\bar{C}$  with  $Cl_2$  in pres. of Al/Hg yields (11) 2,3,6-trichlorotoluene (3:0625);  $\bar{C}$  at its b.p. in u.v. light treated with  $Cl_2$  yields (5) 2,6-dichlorobenzyl chloride (3:0410) cryst. from lgr. or ether, m.p. 39-40° (5).]

[ $\bar{C}$  with  $Br_2$  at 170° in sunlight (2) yields (2) (12) 2,6-dichlorobenzyl bromide which on oxidn. with alk.  $KMnO_4$  yields (2) (12) 2,6-dichlorobenzoic acid (3:4200), m.p. 143-144°.]

$\bar{C}$  on mononitration in cold with 2 pts. fuming  $\text{HNO}_3$  (11) or with mixt. of 2 pts. conc.  $\text{HNO}_3$  ( $D = 1.4$ ) + 3 pts. conc.  $\text{H}_2\text{SO}_4$  at  $100^\circ$  (3) yields 2,6-dichloro-3-nitrotoluene [Beil. V-332], ndls. from alc. +  $\text{AcOH}$ , m.p.  $53^\circ$  (3),  $52-53^\circ$  (11),  $50^\circ$  (13); note that the other possible isomer, viz., 2,6-dichloro-4-nitrotoluene, m.p.  $65^\circ$  (14),  $63-64^\circ$  (15), has been obtd. only by other means. —  $\bar{C}$  on dinitration with mixt. of 7 pts. fuming  $\text{HNO}_3$  ( $D = 1.5$ ) and  $3\frac{1}{2}$  pts. conc.  $\text{H}_2\text{SO}_4$  at  $100^\circ$  yields (3) 2,6-dichloro-3,5-dinitrotoluene [Beil. V-345], ndls. from alc., m.p.  $121-122^\circ$  (3),  $121^\circ$  (4) (14); note that the isomeric 2,6-dichloro-3,4-dinitrotoluene, m.p.  $130-131^\circ$  (14),  $129-130^\circ$  (16), has been obtd. only by other means.

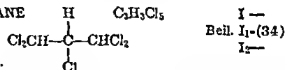
$\bar{C}$  is extremely resistant to oxidn. either with dil.  $\text{HNO}_3$  (9) (1) (3), aq. alk.  $\text{KMnO}_4$  (4) (12), acid  $\text{KMnO}_4$  (12),  $\text{KMnO}_4$  in acetone (4),  $\text{CrO}_3$  in  $\text{H}_2\text{SO}_4$  or  $\text{AcOH}$  (12), or  $\text{K}_2\text{Cr}_2\text{O}_7$  in  $\text{H}_2\text{SO}_4$  (12); by conversion of  $\bar{C}$  with  $\text{Br}_2$  to 2,6-dichlorobenzyl bromide (see above) and oxidn. of this with alk.  $\text{KMnO}_4$  (2) (12) 2,6-dichlorobenzoic acid (3:4200), m.p.  $143-144^\circ$ , is obtd. in 57% yield (12).

$\bar{C}$  on sulfonation with fuming  $\text{H}_2\text{SO}_4$  (3) yields 2,6-dichlorotoluenesulfonic acid-3 (corresp. sulfonyl chloride, m.p.  $60^\circ$  (3) (13), corresp. sulfonamide, m.p.  $204^\circ$  (3) (13),  $199-201^\circ$  u.c. (17));  $\bar{C}$  on treatment with chlorosulfonic acid in  $\text{CHCl}_3$  as directed (17) cf. (18) yields 2,6-dichlorotoluenesulfonyl chloride-3, m.p.  $54-56^\circ$  u.c. (17),  $60^\circ$  (3) (13) (18).

3:6270 (1) Wynne, Greeves, *Proc. Chem. Soc.* 11, 151-152 (1895). (2) Lehmstedt, Schrader, *Ber.* 70, 1530 (1937). (3) Cohen, Dakin, *J. Chem. Soc.* 79, 1131-1133 (1901). (4) Davies, *J. Chem. Soc.* 119, 873 (1921). (5) Austin, Johnson, *J. Am. Chem. Soc.* 54, 657-659 (1932). (6) Geigy and Co., *Ger.* 210,850, June 16, 1909; *Cent.* 1909, II 79-80. (7) Aronheim, Dietrich, *Ber.* 8, 1402 (1875). (8) Schultz, *Ann.* 187, 263 (1877). (9) Claus, Stavenhagen, *Ann.* 269, 231 (1892). (10) Ref. 3, p. 1117.

(11) Cohen, Dakin, *J. Chem. Soc.* 81, 1343, 1346 (1902). (12) Norris, Bearse, *J. Am. Chem. Soc.* 62, 956 (1940). (13) Silvester, Wynne, *J. Chem. Soc.* 1936, 692, 695. (14) Davies, *J. Chem. Soc.* 121, 812, 814 (1922). (15) Levy, Stephen, *J. Chem. Soc.* 1931, 78-79. (16) Davies, Leeper, *J. Chem. Soc.* 1926, 1416. (17) Huntress, Carten, *J. Am. Chem. Soc.* 62, 512-513 (1940). (18) I.G., *Brit.* 281,290, Jan. 25, 1928; *French* 644,319, Oct. 5, 1928; *Cent.* 1929, II 352. (19) Lock, Stach, *Ber.* 76, 1252-1256 (1943).

### 3:6280 1,1,2,3,3-PENTACHLOROPROPANE (*sym.*-Pentachloropropane)



B.P.  
 $198-200^\circ$  (1)  $D_4^{34} = 1.6086$  (1)  $n_D^{25} = 1.5131$  (1)  
 $126^\circ$  at 90 mm. (1)  
 $98-100^\circ$  at 20 mm. (2)

Colorless liq. — Dissolves sulfur and vulcanized rubber.

[For prepn. (yields: 70-75% (3), 63% (2), 46% at  $17^\circ$  for 22 hrs. (3)) from  $\text{CHCl}_3$  (3:5050) + *sym.*-dichloroethylene (3:5030) +  $\text{AlCl}_3$  by stirring with sand for 20 hrs. at  $30^\circ$  see (2) (3) (4)]

$\bar{C}$  with alc.  $\text{KOH}$  (1 mole) gives (70% yield (2)) 1,2,3,3-tetrachloropropene-1 (3:5920), b.p.  $165-167^\circ$  (2).

3:6280 (1) Prins, *J. prakt. Chem.* (2) 89, 421 (1914). (2) Heilbron, Healop, Irving, *J. Chem. Soc.* 1936, 782-783. (3) Porns, Engelhard, *Rac. trav. chim.* 54, 307-312 (1935). (4) Prins, *Ger.* 261,689, July 2, 1913, *Cent.* 1913, II 391; (*C.A.* 7, 3641 (1913)).

## 3:6290 2,4-DICHLOROTOLUENE

 $C_7H_5Cl_2$ 

Beil. V - 295

V<sub>1</sub>-(152)V<sub>2</sub>-(230)

B.P.

F.P.

199.9-200.5° cor. at 760 mm. (1)

-13.5° (1)

 $D_{20}^{20} = 1.2498$  (1)

198-200° (2)

1.24597 (6)

196.4-198.2° (3)

196-197.5° (4)

 $n_D^{22} = 1.5480$  (1)

196-197.0° (5)

194° u.c. at 746 mm. (6)

82.0-82.9° at 16 mm. (3)

For f.p./compn. diagram of system:  $\bar{C}$  + 3,4-dichlorotoluene (3:6355) see (1); the eutectic conts. 48%  $\bar{C}$  and freezes about -38° (1).

[For prepn. of  $\bar{C}$  from 2-chloro-4-aminotoluene [Beil. XII-988, XII<sub>1</sub>-(435)] via diazotization and use of  $Cu_2Cl_2$  reaction (yield: 72% (5), 30% (6)) see indic. refs.; similarly from 4-chloro-2-aminotoluene [Beil. XII-835, XII<sub>1</sub>-(389)] see (2); from 2,4-diaminotoluene [Beil. XIII-124, XIII<sub>1</sub>-(40)] via tetrazotization and use of  $CuCl_2$  reaction (yield: 75% (7), 57% (16), 45% (4)) (3) see indic. refs.; from toluene +  $AlCl_3$  +  $SO_2Cl_2$  at 70° (68% yield) see (10).]

[For formn. of  $\bar{C}$  (58% together with 42% 3,4-dichlorotoluene (3:6355) from *p*-chlorotoluene (3:8237) with  $Cl_2$  in pres. of Fe see (1); for formn. of  $\bar{C}$  (together with other isomers) from toluene with  $Cl_2$  in pres. of  $FeCl_3$  or  $MoCl_5$  (8) or by electrolysis in conc.  $HCl/AcOH$  soln. (9) see indic. refs.; from *o*-chlorotoluene (3:8245) or *p*-chlorotoluene (3:8237) with  $Cl_2$  in pres. of  $FeCl_3$  or  $MoCl_5$  (8) or  $Al/Hg$  (11) see indic. refs.; from potassium salt of 2,4-dichlorotoluenesulfonic acid-5 (12), sodium salt of 2,4-dichlorotoluenesulfonic acid-6 (12), or the sodium salt or amide of 2,4-dichlorotoluenesulfonic acid-3 (12) by hydrolysis in  $H_3PO_4$  with steam at 240° see indic. refs.]

[ $\bar{C}$  with  $Cl_2$  in pres. of Fe (13) or of  $Al/Hg$  (14) yields 2,4,5-trichlorotoluene (3:2100) together with other isomers;  $\bar{C}$  with  $Br_2$  at 180-200° yields (15) 2,4-dichlorobenzal dibromide which upon hydrolysis with conc.  $H_2SO_4$  as directed gives 92% overall yield 2,4-dichlorobenzaldehyde (3:1800), m.p. 74.5° (15) (for similar reaction with  $Cl_2$  see (5)).]

[ $\bar{C}$  with  $AlCl_3$  + phthalic anhydride gives (60% yield (16)) (17) *o*-(2,4-dichloro-5-methyl)benzoyl-benzoic acid, cryst. from hot toluene, m.p. 140° (16); this prod. htd. 2 hrs. at 100° with 20 pts. conc.  $H_2SO_4$  + 0.2 pt.  $H_3BO_3$  ring-closes yielding 2,4-dichloro-1-methylantraquinone, yel. cryst. from  $CHCl_3$ , m.p. 155° (16).]

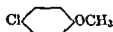
$\bar{C}$  on mononitration, e.g., with cold mixt. of 2 pts. conc.  $HNO_3$  ( $D = 1.42$ ) + 3 pts. conc.  $H_2SO_4$  (2), yields (2) (8) 2,4-dichloro-5-nitrotoluene [Beil. V-332, V<sub>1</sub>-(163)], long hard ndls. from alc., m.p. 54-55° (2), 55° (18), 53° (8), 49-50° (19);  $\bar{C}$  on dinitration, e.g., with 7 pts. fuming  $HNO_3$  ( $D = 1.5$ ) + 3½ pts. conc.  $H_2SO_4$  (2), yields (2) (8) (10) 2,4-dichloro-3,5-dinitrotoluene [Beil. V-345, V<sub>1</sub>-(169)], ndls. from  $MeOH$ , m.p. 104° (2) (18) (10)

$\bar{C}$  on oxidn. with dil.  $HNO_3$  in s.t. at 130-150° (2) (6) (12), with alk.  $KMnO_4$  (70% yield (25)), with  $Na_2Cr_2O_7$  +  $H_2SO_4$  (60% yield (20)), or on electrolytic oxidn. (6.5% yield (21)) gives 2,4-dichlorobenzoic acid (3:4560), m.p. 164°.

$\bar{C}$  on sulfonation with fuming  $H_2SO_4$  yields (2) (22) 2,4-dichlorotoluenesulfonic acid-5 (corresp. sulfonyl chloride, m.p. 72° (22), 71° (2) (24), corresp. sulfonamide, m.p. 176° (2) (22); 175-176° u.c. (23));  $\bar{C}$  on treatment with chlorosulfonic acid in  $CHCl_3$  as directed (23) cf. (24) yields 2,4-dichlorotoluenesulfonyl chloride, m.p. 71-72° u.c. (23), 71° (24).

- 3:6290 (1) Cohen, Da *Monatsh.* 67, 103, 109 (1932). (6) I *J. Chem. Soc.* 1935, 530. (8) Stein, *Ber.* 49, 2481-2487 (1916). (11) Ref. 2, pp. 1116-1117.
- Kopelowitsch, *Arch. Pharm.* 273, 493-495 (1935). (14) Cohen, Dakin, *J. Chem. Soc.* 81, 1340-1341 (1903). (15) Lock, Bock, *Ber.* 70, 923 (1937). (16) Stouder, Adams, *J. Am. Chem. Soc.* 49, 2044-2045 (1927). (17) Adams (to Newport Co.), U.S. 1,711,165, Apr. 30, 1929; *Cent.* 1929, 11 796; *C.A.* 23, 2989 (1929). (18) Blankensma, *Rec. trav. chim.* 29, 415 (1910). (19) Dadswell, Kenner, *J. Chem. Soc.* 1927, 585. (20) Magidsson, Grigorowski, *Russ.* 47,689, July 31, 1936, *Cent.* 1937, 1 430-431.
- (21) Fichter, Adler, *Helv. Chim. Acta* 9, 286 (1926). (22) Silvester, Wynne, *J. Chem. Soc.* 1936, 692. (23) Huntress, Carten, *J. Am. Chem. Soc.* 62, 512-513 (1940). (24) I.G., *Brit.* 281,290, Jan. 25, 1928; *French* 644,319, Oct. 5, 1928; *Cent.* 1929, 11 352. (25) Bornwater, Holleman, *Rec. trav. chim.* 31, 226-230 (1912).

3:6300 *p*-CHLOROANISOLE  
(*p*-Chlorophenyl methyl ether)

 $C_7H_7OCl$ 

Beil. VI - 186  
VI<sub>1</sub>-(101)  
V<sub>2</sub>-(175)

B.P.		B.P. Cont.	
200°	(1) (2) (13)	193-197° u.c.	(7) $D_4^{12.8} = 1.1851$ (11)
198-200°	(3)	94-96° at 25 mm.	(8)
197.5° at 760 mm.	(20)	88° at 18 mm.	(9)
197.7° at 759 mm.	(4)	70.5° at 12 mm.	(10) $n_D^{12.8} = 1.54015$ (11)
190.6-197° at 759 mm.	(5)	74.8-75.4° at 10 mm.	(5)
194-198° u.c.	(6)		

Insol. aq.; eas. sol. alc., ether,  $CHCl_3$ . — Does not freeze at  $-18^\circ$  (3).

[For prepn. from *p*-chlorophenol (3:0475) by methylation with  $Me_2SO_4$  + alk. (7) (6) (1) (60% yield (10)) or with  $MeI$  +  $KOH$  in s.t. at  $120-140^\circ$  (3) see indic. refs.; from anisole (1:7445) +  $PCl_5$  (2) (100% yield (12)) or  $SO_2Cl_2$  (4) see indic. refs.; from *p*-chloroaniline by diazotization and hgt. with  $MeOH$  see (13).]

$\bar{C}$  on mononitration as directed (7) (14) (6) gives (93% yield (6)) 4-chloro-2-nitroanisole [Beil. VI-240], pale yel. lfts. from pet. eth., ndls. or pr. from ale., m.p.  $98.5^\circ$  (15),  $98^\circ$  (14),  $96-97.5^\circ$  (6),  $96^\circ$  (7). [The principal dinitration product, 4-chloro-2,6-dinitroanisole [Beil. VI-260] (best prepd. (16) by further nitration of the 2-nitro prod.), has m.p.  $66^\circ$  (16),  $65^\circ$  (17),  $64^\circ$  (18).]

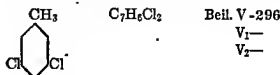
$\bar{C}$  on hgt. with conc.  $HCl$  in s.t. (12) or with  $NaOMe$  in  $MeOH$  in s.t. at  $176^\circ$  (21) gives  $MeCl$  (3:7005) + *p*-chlorophenol (3:0475). (For study of rate of splitting by acids see (19).]

Ⓢ 5-Chloro-2-methoxybenzenesulfonamide: m.p.  $154^\circ$  (22),  $150-151^\circ$  (23). [From  $\bar{C}$  + chlorosulfonic acid followed by conversion of the resultant sulfonyl chloride, m.p.  $104^\circ$  (22), to sulfonamide with  $(NH_4)_2CO_3$ ; 82% yield (23).]

- 3:6309 (1) von Auwers, Baum, Lorenz, *J. prakt. Chem.* 2 (115, 89 (1927). (2) Henry, *Ber.* 2, 710 (1869). (3) Beilstein, Kurbatov, *Ann.* 176, 30 (1875). (4) Peratoner, Ortoleva, *Gazz. chim. Ital.* 28, I 226 (1898). (5) Reitz, Ypsilanti, *Monatsh.* 66, 305 (1935). (6) Ingold, Smith, Yass, *J. Chem. Soc.* 1927, 1248. (7) Kohn, Kramer, *Monatsh.* 49, 151 (1928). (8) Hayashi, *J. prakt. Chem.* (2) 123, 297 (1929). (9) Jones, *J. Chem. Soc.* 1942, 419. (10) Bergmann, Engel, *Z. physik. Chem. B-15*, 95-96 (1931).
- (11) von Auwers, *Z. physik. Chem.* A-158, 418 (1932). (12) Autenrieth, *Arch. Pharm.* 233, 31-32 (1895). (13) Cameron, *Am. Chem. J.* 20, 241 (1898). (14) Reverdin, Eckhard, *Ber.* 32, 2623 (1899). (15) Reverdin, *Ber.* 29, 2599 (1896). (16) Schouten, *Rec. trav. chim.* 66, 555 (1937).

(17) van de Vliet, *Rec. trav. chim.* **43**, 622 (1924). (18) Ref. 7, pp. 154-155. (19) Ghaswalla, Donnan, *J. Chem. Soc.* 1936, 1341-1346. (20) Paulsen, *Monatsh.* **72**, 257 (1939). (21) de Lange, *Rec. trav. chim.* **38**, 103 (1918). (22) Gauntlett, Smiles, *J. Chem. Soc.* 127, 2745 (1925). (23) Huntress, Carten, *J. Am. Chem. Soc.* **62**, 603-604 (1940).

## 3:6310 3,5-DICHLOROTOLUENE



## B.P.

## M.P.

201-202° cor. at 760 mm. (1)	26-27° (10)	$n_D^{20} = 1.5438$ (12)
200° at 750 mm. (2)	26° (2) (3) (5) (7)	
195° at 729 mm. (3)	24.8-25.0° (4)	
78-79° at 9 mm. (12)	24.5° (12)	

Sublimes at ord. temp. (3).

[For prepn. of  $\bar{\text{C}}$  from 3,5-dichloro-2-aminotoluene [Beil. XII-837] via diazotization and reactn. with alc. (yield: 80-85% (2), 57% (5)) (1) see indic. refs.; similarly from 3,5-dichloro-4-aminotoluene [Beil. XII-990] see (3) (4); for formn. of  $\bar{\text{C}}$  from 3,5-dibromo-2-aminotoluene [Beil. XII-840, XII-1(390)] or from 3,5-dibromo-4-aminotoluene [Beil. XII-993, XII-1(437)] by diazotization followed by treatment with HCl gas in alc. see (6); for prepn. from 3,5-dichloro-2-acetaminotoluene by hydrolysis with EtOH/HCl followed by  $\text{HNO}_2$  (34% yield) see (12).]

[ $\bar{\text{C}}$  with  $\text{Cl}_2$  in pres. of Al/Hg gives (7) exclusively 2,3,5-trichlorotoluene (3:0610), m.p. 43-45° (7);  $\bar{\text{C}}$  with  $\text{Cl}_2$  at 180-190° for 10-12 hrs. gives (2) 3,5-dichlorohenzal dichloride (3:0370).]


[ $\bar{\text{C}}$  with  $\text{Br}_2$  in pres. of Fe gives in cold (70% yield (8)) 2-bromo-3,5-dichlorotoluene, ndls. from alc., m.p. 33.5° (8).]

$\bar{\text{C}}$  on mononitration by soln. in ice-cold fuming  $\text{HNO}_3$  ( $D = 1.52$ ) (9) yields 3,5-dichloro-2-nitrotoluene [Beil. V-331], ndls. from alc. + AcOH, m.p. 61-62° (5) (crude prod. m.p. 57° (9));  $\bar{\text{C}}$  on dinitration with mixt. of 4 pts.  $\text{HNO}_3$  ( $D = 1.5$ ) + 4 pts. conc.  $\text{H}_2\text{SO}_4$  (5) or the above mononitro deriv. on further nitration with  $\text{HNO}_3$  ( $D = 1.52$ ) at 65° (9) yields 3,5-dichloro-2,6-dinitrotoluene, ndls. from alc., m.p. 99-100° (5); note that the crude dinitration prod. often melts about 90° (9), probably because of contamination with 3,5-dichloro-2,4-dinitrotoluene, m.p. 127° (9).

$\bar{\text{C}}$  on oxidn. with dil.  $\text{HNO}_3$  (5) (10) in s.t. at 170° (3) yields 3,5-dichlorobenzoic acid (3:4840), m.p. 188°.

$\bar{\text{C}}$  on sulfonation with fuming  $\text{H}_2\text{SO}_4$  yields (5) (11) 3,5-dichlorotoluenesulfonic acid-2, (corresp. sulfonyl chloride, m.p. 44-45° (5) (11), corresp. sulfonamide, m.p. 168-169° (5) (11)).

3:6310 (1) Wynne, Greeves, *Proc. Chem. Soc.* **11**, 151-152 (1895). (2) Asinger, Lock, *Monatsh.* **62**, 345 (1933). (3) Lellmann, Klotz, *Ann.* **231**, 323-324 (1885). (4) Maryott, Hobbs, Gross, *J. Am. Chem. Soc.* **62**, 2321 (1940). (5) Cohen, Dakin, *J. Chem. Soc.* **79**, 1133-1134 (1901). (6) Hantzsch, *Ber.* **30**, 2344-2346 (1897). (7) Cohen, Dakin, *J. Chem. Soc.* **81**, 1343-1344 (1902). (8) Asinger, *J. prakt. Chem.* **179**, 300 (1894). (9) Borsche, Trautner, *Ann.* **447**, 13 (1926). (10) Asinger, *J. prakt. Chem.* **179**, 300 (1894). (11) Marvel, Overberger, Allen, Johnston, *J. Am. Chem. Soc.* **70**, 2441 (1948). (12) Marvel, Overberger, Allen, Johnston, *J. Am. Chem. Soc.* **70**, 2441 (1948).

3:6312 HEXACHLOROPROPANONE-2  $\text{Cl}_3\text{C}-\text{C}(\text{Cl})_2-\text{COCl}_2$   $\text{C}_3\text{OCl}_6$  Beil. I - 657  
(Hexachloroacetone)   $\text{I}_1-$   
 $\text{I}_2-$

B.P. F.P.  
202-204° (1) (7) -2° (1)  $D_{12}^{12} = 1.744$  (1) (7)  
110° at 40 mm. (2) -3 to -4° (2)

[See also pentachloropropanone-2 (3:6205).]


Colorless limpid liq. with odor which although faint at low temp. becomes sharp and lachrymatory at higher temps. —  $\bar{\text{C}}$  is spar. aol. aq. but with it forms a cryst. monohydrate, m.p. + 15°, alm. insol. aq.

[For prepn. of  $\bar{\text{C}}$  from acetone (1:5400) in 90% AcOH + a little HCl with  $\text{Cl}_2$  for 12 hrs. at room temp., followed (after addn. of NaOAc) by 40 hrs. further chlorination at b.p. (2), or with  $\text{Cl}_2$  in sunlight (1) (some pentachloroacetone (3:6205) is formed by either method): for prepn. of  $\bar{\text{C}}$  from chloroacetone (3:5425) with  $\text{Cl}_2$  at 50-100° in light (3) (4) or under press. (5) see indic. refs.; for formn. of  $\bar{\text{C}}$  from citric acid (1:0455) in conc. aq. soln. with  $\text{Cl}_2$  in sunlight (1) (6) (7), or from glycerol (1:6540) with  $\text{Cl}_2$  in pres. of  $\text{I}_2$  (7), see indic. refs.]

$\bar{\text{C}}$  on stdg. with aq. at 30° (2) or with aq. in s.t. at 120° (1) readily undergoes hydrolytic cleavage yielding chloroform (3:5050) and trichloroacetic acid (3:1150).

$\bar{\text{C}}$  with conc. aq.  $\text{NH}_4\text{OH}$  readily splits yielding (1) chloroform (3:5050) and trichloroacetamide, spar. sol. aq., m.p. 141°; similarly  $\bar{\text{C}}$  with aniline yields (1) chloroform (3:5050) and trichloroacetanilide, m.p. 95-97°.

3:6312 (1) Cloëz, *Ann. chim.* (6) 9, 199-205 (1886) (2) Edwards, Evans, Wilson, *J. Chem. Soc.* 1937, 1944-1945. (3) Hiesel, Hendschel (to I.G.), U.S. 2,199,934, May 7, 1940; *C.A.* 34, 5855 (1940). (4) I.G., French 816,956, Aug. 21, 1937, *Cent.* 1938, I 2216. (5) I.G., French 837,741, Feb. 20, 1939; *Cent.* 1939, II 228. (6) Städel, *Ann.* 111, 299-300 (1859). (7) Cloëz, *Ann.* 122, 119-122 (1862). (8) Zaharia, *Cent.* 1896, I 100

— DI-(TRICHLOROMETHYL) CARBONATE  $\text{OCCl}_3$   $\text{C}_3\text{O}_2\text{Cl}_6$  Beil. III - 17  
  $\text{III}_1-(8)$   
 $\text{III}_2-(16)$

B.P. 203° at 760 mm. M.P. 78-79°

See 3:1915. Division A: Solids.

3:6315 *n*-BUTYL TRICHLOROACETATE  $\text{C}_4\text{H}_9\text{O}_2\text{Cl}_3$  Beil. S.N. 160  
 $n\text{-C}_4\text{H}_9\text{O.CO.CCl}_3$

B.P. 203-205° (1)  $D_4^{25} = 1.266$  (3)  $n_D^{25} = 1.4495$  (3)  
111° at 40 mm. (2)  
100-101° at 24 mm. (3)  $D_4^{20} = 1.2778$  (4)  $n_D^{20} = 1.4525$  (4)

[For prepn. (82-89% yield (3), 98% yield (2)) from *n*-butyl alc. (1:6180) + trichloroacetic ac. (3:1150) see (2) (3).]

3:6315 (1) Cheng, *Z. physik. Chem. B-24*, 308 (1934). (2) Liston, Dehn, *J. Am. Chem. Soc.* 60, 1264-1265 (1938). (3) Waddle, Adkins, *J. Am. Chem. Soc.* 61, 3361-3364 (1939). (4) Schjanberg, *Z. physik. Chem. A-172*, 229 (1935).

**3:6317 TRICHLOROACETALDEHYDE DIETHYLACETAL**  $C_6H_{11}O_2Cl_3$  Beil. I-021  
 ( $\beta,\beta,\beta$ -Trichloroacetal)  $Cl_3C-CH(OC_2H_5)_2$  I<sub>1</sub>-  
 (Chloral diethylacetal) I<sub>2</sub>-

B.P. 204.8° at 758.7 mm. (1)  $D_{25}^{15.2} = 1.2055$  (1)  
 197° (2)  
 84-85° at 10 mm. (3)

Colorless oil, spar. sol. aq. (abt. 5 g.  $\bar{C}$  per liter aq. (2)), but misc. with alc., ether, or glycerol.

[For prepn. of  $\bar{C}$  from ethyl  $\alpha,\beta,\beta,\beta$ -tetrachloroethyl ether [Beil. I-623, I<sub>2</sub>-(681)] (itself prepd. (25-33% yield (3)) cf. (7) from chloral ethylalcoholate (3:0860) with  $PCl_3$  by protracted boilg. (4) (5) (1) with abs. alc. (70% yield (3)) see indic. refs.; for formn. of  $\bar{C}$  from chloral ethylalcoholate (3:0860) with  $Cl_2$  at 80° (2), or from 75% ethyl alc. with  $Cl_2$  (2), see indic. refs.]

$\bar{C}$  above 200° or on distn. with conc.  $H_2SO_4$  yields (2) anhydrous chloral (3:5210).

$\bar{C}$  is stable toward alkalis (2) and is unattacked by  $HCl$  gas even at 150° (6).

[ $\bar{C}$  with  $K$  *ter*-butylate in *ter*-butyl alc. splits out  $HCl$  giving (76% yield (3)) dichloro-keteno diethylacetal, b.p. 177° at 732-740 mm.,  $D_{25}^{25} = 1.1672$ ,  $n_D^{25} = 1.4350$  (3).]

**3:6317** (1) Paterno, Pisati, *Gazz. chim. ital.* 2, 333-338 (1872). (2) Byasson, *Compt. rend.* 87, 26 (1878); *Bull. soc. chim.* (2) 32, 304-305 (1879). (3) Magnani, McElvain, *J. Am. Chem. Soc.* 60, 2211-2212 (1938). (4) Wurtz, Frapollis, *Jahresber.* 1872, 438. (5) Wurtz, Vogt, *Zeit für Chemie*, 1871, 680. (6) Jacobsen, Neumeister, *Ber.* 15, 602 (1882). (7) Post, *J. Org. Chem.* 6, 833 (1941).

**3:6318  $\beta,\beta'$ -DICHLORO-ISOPROPYL ACETATE**  $C_6H_8O_2Cl_2$  Beil. II - 130  
 (Glycerol  $\alpha,\alpha'$ -dichlorohydrin  $CH_2Cl$  II<sub>1</sub>-(59)  
 $\beta$ -acetate,  $\beta$ -aceto- $\alpha,\gamma$ -dichlorohydrin)  $HC-O.CO.CH_3$  II<sub>2</sub>-(140)  
 $CH_2Cl$

B.P. 205° (1) at 760 mm. (2)  $D_{25}^{25} = 1.267$  (0)  $n_D^{25} = 1.4513$  (6)  
 202-208° (3)  
 204° (13)  $D_{20}^{20} = 1.281$  (9)  $n_D^{20} = 1.4555$  (7)  
 202-203° at 740 mm. (4) 1.4542 (9)  
 104-105° u.c. (11)  
 103-105° (9)  
 115-120° at 40 mm. (5)  
 108-119° at 40 mm. (6)  
 87-89° at 12 mm. (7)  
 86° at 12 mm. (8)  
 84.5° at 8 mm. (10)

[See also  $\beta,\gamma$ -dichloro-*n*-propyl acetate (3:6220).]

[For prepn. of  $\bar{C}$  from 1,3-dichloropropanol-2 ("  $\alpha$ -dichlorohydrin ") (3:5985) with  $AcCl$  (3:7065) under reflux (11) (9) (15) (3) or with  $Ac_2O$  (1:1015) (12) (13) in pres. of a trace of  $H_2SO_4$  (8) see indic. refs.]

[For prepn. of  $\bar{C}$  from 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358) with  $AcCl$  (3:7065) (73% yield (7)) in s.t. at 100° for 2 hrs. (10) or 30 hrs. (4) or with  $Ac_2O$  (1:1015) in s.t. at 180° for 4 hrs. (4) or in pres. of anhydrous  $FeCl_3$  at ord. temp. for 24 hrs. (90% yield (14)) see indic. refs.]

[For formn. of  $\bar{C}$  from glycerol (1:6540) with  $\text{AcCl}$  (3:7063) (1) or with  $\text{AcOH}$  (1:1010) +  $\text{HCl}$  gas at  $100^\circ$  (1) or from glyceryl triacetate (triacetin) with  $\text{HCl}$  gas (5) see indic. refs.]

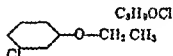
[ $\bar{C}$  with  $\text{MeOH}$  contg. 1%  $\text{HCl}$  at  $60^\circ$  for 6 hrs. gives (85% yield (7)) 1,3-dichloropropanol-2 ("α-dichlorohydrin") (3:5985); for study of rate of hydrolysis of  $\bar{C}$  with  $\text{N}/10$   $\text{HCl}$  see (15)]

$\bar{C}$  with  $\text{K}$  phthalimide at  $150\text{--}170^\circ$  for  $\frac{1}{2}$  hr., then extracted with  $\text{AcOH}$ , gives (3) β,β'-bis-(phthalimido)isopropyl acetate, m.p.  $191^\circ$  (3).

3:6318 (1) Berthelot, de Luca, *Ann. chim.* (3) 52, 459-460 (1858). (2) Gibson, *J. Soc. Chem. Ind.* 50, 950 (1931). (3) Fairbourn, Cowdrey, *J. Chem. Soc.* 1929, 133-134. (4) Truchot, *Compt. rend.* 61, 1171 (1865), *Ann.* 138, 297-299 (1868); 140, 244-246 (1866). (5) De La Aenza, *Compt. rend.* 139, 668 (1904). (6) Gibson, *J. Soc. Chem. Ind.* 50, 973 (1931). (7) Sjöberg, *Svensk Kem. Tid.* 53, 454-457 (1911); *Cent.* 1912, H<sub>2</sub>25, C.A. 37, 4363 (1913). (8) Wegscheider, *Zentralbl. Monatsh.* 34, 1075 (1913). (9) Humnick, *Bull. soc. chim.* (4) 45, 280 (1929). (10) Abderhalden, Weil, *Fermentforschung* 4, 64 (1920), *Cent.* 1920, H<sub>2</sub> 643.

(11) Henry, *Ber.* 4, 704 (1871). (12) Seelig, *Ber.* 24, 3479 (1891). (13) Bigot, *Ann. chim.* (6) 22, 492-493 (1891). (14) Knoevenagel, *Ann.* 402, 134-138 (1914). (15) Bancroft, *J. Am. Chem. Soc.* 41, 425, 429 (1919).

3:6323 *m*-CHLOROPHENETOLE  
(*m*-Chlorophenyl ethyl ether)



B.P.

201-205° cor. at 717 mm. (1)

201-205° (2)

$D_4^{20} = 1.1712$  (1)

Colorless oil with agreeable odor. — Gas. sol. alc., ether,  $\text{AcOH}$ ,  $\text{C}_6\text{H}_6$ .

[For prepn. of  $\bar{C}$  from *m*-chlorophenol (3:0255) with  $\text{EtI}$  +  $\text{KOH}$  on alc. in a.t. at  $100^\circ$  for 3 hrs. see (1).]

[ $\bar{C}$  with  $\text{HCN}$  +  $\text{C}_6\text{H}_6$  +  $\text{AlCl}_3$  at room temp. for 2 hrs. followed by hydrolysis gives (50% yield (2)) 2-chloro-4-ethoxybenzaldehyde [Beil. VIII-81], m.p.  $66.5^\circ$  (2).]

The direct nitration of  $\bar{C}$  has not been reported. [Note, however, that all 4 possible mononitration products are known: viz., 3-chloro-2-nitrophenetole, m.p.  $52^\circ$  (3); 3-chloro-4-nitrophenetole, m.p.  $39\text{--}40^\circ$  (3); 3-chloro-5-nitrophenetole, m.p.  $47^\circ$  (4); and 3-chloro-6-nitrophenetole, m.p.  $63^\circ$  (3) (5),  $62\text{--}63^\circ$  (6). — The only known dinitro-derivative of  $\bar{C}$  is 3-chloro-1,6-dinitrophenetole [Beil. VI-259], m.p.  $112^\circ$  (7) (8). — The only known trinitro-derivative of  $\bar{C}$  is 3-chloro-2,4,6-trinitrophenetole [Beil. VI-292], m.p.  $61^\circ$  (5). — All 6 of these nitro products were obtained indirectly.]

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— 2,5-DICHLOROPHENOL



Beil. VI —

VI<sub>1</sub>-(102)

VI<sub>2</sub>—

B.P. 206°

M.P. 58°

See 3:1172 *Disinfectants: Solids*



3:6327 BENZAL (DI)CHLORIDE  
(Benzylidene (di)chloride,  
 $\alpha,\alpha$ -dichlorotoluene;  
 $\omega,\omega$ -dichlorotoluene)



Beil. V - 297

V<sub>1</sub>-(152)V<sub>2</sub>-(232)

B.P.

[207° cor.

F.P.

(1)] -16.0° to -16.2° cor. (9)  $D_4^{14} = 1.2557$  (1)

-16.1°

cor. (10)

 $n_D^{20} = 1.5503$  (3)

205.2° at 760 mm. (2)

-16.4°

(11)

1.5502 (13)

205.15° at 760 mm. (3)

-17.0°

(12)

205° (37)

-17.4°

(2)

 $D_4^{14} = 1.2699$  (4)

203.5° at 766.2 mm. (4)

(5)

 $n_D^{19.4} = 1.5515$  (14)

203.5° (5)

See Note 2. See Note 3.

201° (6)

118° nt 60 mm. (7)

Note 1. The b.p. of 214° given by (15) appears without justification.

104-105° nt 30 mm. (8)

Note 2.  $D_4^{56.8} = 1.2122$  (4);  $D_4^{79.2} = 1.1877$  (4);  
 $D_4^{135.5} = 1.1257$  (4).

See Note 1.

Note 3. The value of  $n_D^{20}$  for mixtures of  $\bar{C}$  with benzyl chloride (3:8535) ( $n_D^{20} = 1.5391$  (13)) is a linear function of their composition (13).

[See also benzyl chloride (3:8535) and benzotrichloride (3:6540).]

Ordinary comm.  $\bar{C}$ , usually obtd. by chlorination of toluene, frequently conts. benzyl chloride (3:8535) and benzotrichloride (3:6540), which are difficult (if not impossible) to remove by distillation methods. For purification of  $\bar{C}$  by repeated fractional freezing see (5); for patent on purification of  $\bar{C}$  from inorganic contaminants see (16). The best approach to pure  $\bar{C}$  is from benzaldehyde by action of PCl<sub>5</sub> (see below).

$\bar{C}$  is insol. aq.; sol. alc., ether, or below -20° in equal vol. of pet. ether (17).

[For a method for quant. detn. of  $\bar{C}$  in mixtures with benzyl chloride (3:8535) and benzotrichloride (3:6540) see (18); for a rapid combustion method for detn. of chlorine in  $\bar{C}$  see (19).]

### PREPARATION OF $\bar{C}$

From benzaldehyde. [For prepn. of  $\bar{C}$  from benzaldehyde (1:0195) with PCl<sub>5</sub> (yield: 80-85% (20)) (21) in CHCl<sub>3</sub> (9), with POCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> (22), with SOCl<sub>2</sub> (23) (24), with COCl<sub>2</sub> (3:5000) in s.t. at 120-130° (25), with oxalyl (di)chloride (3:5060) in s.t. at 130-140° for 2 hrs. (26), or with succinyl (di)chloride (3:6200) in s.t. at 100° (27) see indic. refs.]

From toluene. [For prepn. of  $\bar{C}$  from toluene (1:7405) with SO<sub>2</sub>Cl<sub>2</sub> (2 moles) in presence of a trace of dibenzoyl peroxide refluxed for 6 hours (90% yield (8)), with SOCl<sub>2</sub> in s.t. at 230-250° (28), with PCl<sub>5</sub> in s.t. at 190-195° for 2 hours (29), or with NOCl at 350° (30) see indic. refs.]

[For studies of formn. of  $\bar{C}$  from toluene (1:7405) with Cl<sub>2</sub>, especially in light, see the scientific papers (13) (31) (32) (33) and patents (34) (35) (36).]

From other sources. [For formn. of  $\bar{C}$  from benzyl chloride (3:8535) with Cl<sub>2</sub> (37) (38), with NOCl at 150° (39), or with PbCl<sub>2</sub>·2NH<sub>4</sub>Cl (40) see indic. refs.; from various benzyl ethers by cleavage with PCl<sub>5</sub> see (41); from  $\alpha$ -chlorobenzyl chloroformate [Beil. VII-211] by loss of CO<sub>2</sub> on distn. see (42); or from benzaldazine with NOCl see (43).]

CHEMICAL BEHAVIOR OF  $\tilde{C}$ 

**Pyrolysis.** [ $\tilde{C}$  passed over red-hot Pt wire gives (44) HCl and both *cis* (3:1380) and *trans* (3:4210) toluene dichlorides ( $\alpha, \alpha'$ -dichloro- $\alpha, \alpha'$ -diphenylethylenes).]

**Reduction.** [ $\tilde{C}$  with  $H_2$  in pres. of Pd/CaCO<sub>3</sub> (45) or Ni (46) in alc. KOH loses all its halogen as HCl (use in quant. detn.) but the corresp. org. reduction prod. has not been characterized. —  $\tilde{C}$  with  $H_2$  in pres. of colloidal Pd in dil. alc. gives (47) toluene (1:7405), benzyl chloride (3:8535), and  $\alpha$ -stilbene dichloride (3:4854). —  $\tilde{C}$  in MeOH/KOH with hydrazine hydrate in pres. of Pd gives (10% yield (48))  $\alpha$ -stilbene dichloride (3:4854).]

**Hydrolysis.**  $\tilde{C}$  upon hydrolysis yields benzaldehyde (1:0195) and HCl; frequently the reaction is so executed that the benzaldehyde reacts further according to the nature of the environment; examples of both types of reaction are cited below.

[ $\tilde{C}$  with aq. in s.t. at 140–160° (1), with aq. in pres. of ferric salts (49) or metallic Fe (50) below 100°, with 50% aq. acetone at 72° (59), with conc. H<sub>2</sub>SO<sub>4</sub> (2 moles) at 50° subsequently poured into aq. (51), with H<sub>3</sub>BO<sub>3</sub> (1 mole) at 130–160° (52) (note that benzyl chloride (3:8535) is unaffected while benzotrichloride (3:6540) gives benzoic acid (1:0715)), with boilg. aq. K<sub>2</sub>CO<sub>3</sub> (53), with moist NiCO<sub>3</sub> at 120° or moist CoCO<sub>3</sub> at 60° for 3 hrs. (60), with aq. Na<sub>2</sub>SO<sub>3</sub> at 110° (54), with ZnO in C<sub>6</sub>H<sub>6</sub> followed by aq. (55), with anhydrous formic acid (56) (57), or with anhydrous oxalic acid at 130° (58) gives (yields: 85% (52), 82% (58), 79% (51), 76% (60), 75% (59), 70% (54), 30% (55)) benzaldehyde (1:0195).]

[For study of kinetics of hydrolysis of  $\tilde{C}$  at 30° and 60° in aq. acetone either directly or in pres. of H<sub>2</sub>SO<sub>4</sub> or KOH see (61), with aq. or KOH in 95% alc. see (62); for study of influence of substituents on hydrolysis of  $\tilde{C}$  see (61) (63) (64).]

[ $\tilde{C}$  with AcOH + ZnCl<sub>2</sub> gives (65) benzaldehyde (1:0195) + acetyl chloride (3:7065) + HCl. —  $\tilde{C}$  with anhydrous alkali acetate at 180–200° for 10–20 hrs. gives (66) cinnamic acid (1:0735). —  $\tilde{C}$  with AgOAc (32) (1) (67) or with PhO in AcOH (68) gives benzal diacetate [Beil. VII-210, VII<sub>1</sub>-(119)], m.p. 45–46°.]

**Alcoholysis.** [ $\tilde{C}$  with EtOH + ZnCl<sub>2</sub> gives (65) benzaldehyde (1:0195) + ethyl chloride (3:7015) + HCl; an analogous reaction occurs with  $\tilde{C}$  + ZnCl<sub>2</sub> + aromatic alcohols (69). —  $\tilde{C}$  with sodium alcoholates under ord. press. gives the corresp. benzaldehyde acetals; e.g.,  $\tilde{C}$  with MeOH/NaOMe at 100° for 15 hrs. gives (15% yield (70)) (67) benzaldehyde dimethylacetal [Beil. VII-209], b.p. 194–196°;  $\tilde{C}$  with EtOH/NaOEt at 100° for 24 hrs. gives (33% yield (70)) (67) benzaldehyde diethylacetal [Beil. VII-209, VII<sub>1</sub>-(119)], b.p. 222°. — However,  $\tilde{C}$  with sodium alcoholates under press. in s.t. gives (70) benzaldehyde (1:0195) together with the corresp. alkyl chlorides.]

**Substitution. Chlorination** [ $\tilde{C}$  with Cl<sub>2</sub> in pres. of I<sub>2</sub> gives (32) *p*-chlorobenzal (di)chloride (3:6700). — Note, however, that  $\tilde{C}$  with excess liquid Cl<sub>2</sub> in s.t. in sunlight gives (71) an addn. prod., viz., benzal (di)chloride hexachloride, m.p. 153° (71); also that  $\tilde{C}$  with NOCl at 150° substitutes in the side chain giving (39) benzotrichloride (3:6540). — Note further that  $\tilde{C}$  with SO<sub>2</sub>Cl<sub>2</sub> + dibenzoyl peroxide does not react even when refluxed for 20 hrs. (8); cf. prepn. of  $\tilde{C}$  from toluene by this method (above).]

**Bromination.** [ $\tilde{C}$  with Br<sub>2</sub> in pres. of metallic beryllium gives (72) *p*-bromobenzal (di)bromide, b.p. 170–171° at 10 mm. (72). —  $\tilde{C}$  with Br<sub>2</sub> at 120–140° gives (57) benzodichloride bromide, C<sub>6</sub>H<sub>4</sub>CCl<sub>2</sub>Br, b.p. 88–94° at 1 mm., and benzochloride dibromide, C<sub>6</sub>H<sub>4</sub>OCIBr<sub>2</sub>, b.p. 98–103° at 1 mm.]

**Sulfonation.** [ $\tilde{C}$  with SO<sub>3</sub> does not sulfonate but instead undergoes hydrolysis: e.g.,  $\tilde{C}$  with sulfuric acid monohydrate at 35° gives (73) a mixt. of benzaldehyde-sulfonic acids in the ratio 10% *o*- + 30% *m*- + 60% *p*-, although these products cannot be isolated as such.]

**Nitration.** [All three isomeric mononitro derivatives of  $\tilde{C}$  are known, viz., *o*-nitrobenzal (di)chloride [Beil. V-332, V<sub>1</sub>-(163)], m.p. 27.5° (63), 26–26.5° (61), 25.7° (11); *m*-nitrobenzal (di)chloride [Beil. V-332, V<sub>1</sub>-(163), V<sub>2</sub>-(254)], m.p. 64.5–65° (61), 64.5° (11); *p*-nitrobenzal

(di)chloride [Beil. V-332, V<sub>1</sub>-(163), V<sub>2</sub>-(255)], m.p. 43.0–43.5° (61), 43° (63), 42.8° (11); however, they are best prepared by reaction of the corresp. nitrobenzaldehydes with PCl<sub>5</sub> (74) (75). — For thermal anal. of mixtures of the three nitrobenzal (di)chlorides see (11). — For study of the mononitration of  $\bar{C}$  with anhydrous HNO<sub>3</sub> in Ac<sub>2</sub>O at 20° giving about 23% o- + 34% m- + 43% p- see (11) cf. (76). — Note that neither dinitro nor trinitro derivatives of  $\bar{C}$  have been reported.]

**Behavior with other inorganic reactants.  $\bar{C}$  with metals.** [ $\bar{C}$  with Na on htg gives (1) stilbene (1:7250). For behavior of  $\bar{C}$  with Na in liq. NH<sub>3</sub> giving dibenzyl, benzylamine, and other products see (80). —  $\bar{C}$  with equal wt. of Cu powder at 100° for 12 hrs. couples with loss of 2 Cl giving (77)  $\alpha$ -stilbene dichloride (3:4854). —  $\bar{C}$  on boiling with Cu in aq. Na<sub>2</sub>CO<sub>3</sub> for 24 hrs. gives (78) benzaldehyde-copper, 2C<sub>6</sub>H<sub>5</sub>.CHO.Cu, green cryst., decg. about 220° without melting. —  $\bar{C}$  with Cu in pyridine reacts vigorously (79), but the products have not been characterized.]

**$\bar{C}$  with inorganic salts.** [ $\bar{C}$  with AlCl<sub>3</sub> in pet. eth. or CS<sub>2</sub> evolves HCl and resinifies (37);  $\bar{C}$  with very small amt. AlCl<sub>3</sub> at -15° gives (small yield (81)) phenyl-*m*-dichloromethyl-phenylchloromethane, b.p. 285° at 750 mm.]

[ $\bar{C}$  with SbF<sub>3</sub> on htg gives (82) (83) benzal (di)fluoride [Beil. V-290, V<sub>1</sub>-(149), V<sub>2</sub>-(224)], b.p. 130.95° (83),  $D_4^{20} = 1.13572$  (84),  $n_D^{20} = 1.45775$  (84).]

[ $\bar{C}$  with alc. Na<sub>2</sub>S under N<sub>2</sub> gives (85) cf. (86) monomeric thiobenzaldehyde, but this cannot be isolated since it immediately undergoes polymerization to  $\beta$ -trithiobenzaldehyde and/or other reactions. —  $\bar{C}$  with alc. NaSH refluxed 3–4 hrs. gives (86) dibenzyl disulfide [Beil. VI-465, VI<sub>1</sub>-(229), VI<sub>2</sub>-(437)], m.p. 69–70° (86).]

[ $\bar{C}$  with conc. aq. NH<sub>4</sub>OH on stdg. 4 months at ord. temp. (87), or  $\bar{C}$  with alc. NH<sub>4</sub>OH in s.t. at 100° (88), or  $\bar{C}$  with alc. NH<sub>4</sub>OH + trace of Zn dust at room temp. (88), gives hydrobenzamide [Beil. VII-215, VII<sub>1</sub>-(120)], m.p. 119°, doubtless through intermediate hydrolysis to benzaldehyde since this can sometimes (88) be isolated.]

**Behavior with organic reactants.  $\bar{C}$  with hydrocarbons.** [ $\bar{C}$  with C<sub>6</sub>H<sub>6</sub> in pres. of AlCl<sub>3</sub> (37) (89), Cr (90), BeCl<sub>2</sub> at 130–140° for 20 hrs. (91), or Zn dust (92) undergoes Friedel-Crafts reaction giving (yields: 28.7% (91), 19.5% (90), 13.4% (37)) triphenylmethane (1:7220) frequently accompanied (37) (89) by other products such as diphenylmethane (1:7120) and triphenylchloromethane (3:3410). —  $\bar{C}$  with C<sub>6</sub>H<sub>6</sub> + Al + HgCl<sub>2</sub> at 50–55° gives (93) cf. (89) 9,10-diphenyl-9,10-dihydroanthracene [Beil. V-745, V<sub>2</sub>-(681)], m.p. 164° (89), 159° (93).]

[ $\bar{C}$  with toluene in pres. of BeCl<sub>2</sub> refluxed 3 hrs. gives (73% yield (91)) phenyl-di-*p*-tolylmethane (4,4'-dimethyl-triphenylmethane) [Beil. V-712, V<sub>1</sub>-(352), V<sub>2</sub>-(623)], accompanied by other products. —  $\bar{C}$  with toluene + Al + HgCl<sub>2</sub> at 60–70° for 2 hrs. gives (93) a hydrocarbon C<sub>26</sub>H<sub>24</sub>, m.p. 185°, possibly having the structure 9,10-di-*p*-tolyl-9,10-dihydroanthracene.]

[ $\bar{C}$  with *o*-xylene (1:7430) + AlCl<sub>3</sub> in acetylene tetrachloride (3:6750) as solvent gives (very small yield (94)) 2,3,6,7-tetramethyl-9,10-diphenylanthracene, m.p. 312°; note that this product has composition C<sub>30</sub>H<sub>26</sub> and is *not* a dihydroanthracene deriv.]

[For use of  $\bar{C}$  + conc. H<sub>2</sub>SO<sub>4</sub> as a color test for various aromatic hydrocarbons see (95) (96).]

**$\bar{C}$  with phenols.** [ $\bar{C}$  with phenol at 120° for 10 hrs. condenses with loss of HCl giving (87% yield (70)) 4,4'-dihydroxy-triphenylmethane (leucobenzaurin) [Beil. VI-1042, VI<sub>1</sub>-(1010)], ndls. from aq. alc. or from ClICH<sub>3</sub>, m.p. 160–161° (corresp. diacetate, m.p. 115° (97)); this prod. is also ohtd. from benzaldehyde (1:0195) by condensation with phenol (1:1420) in pres. of H<sub>2</sub>SO<sub>4</sub> (yields: 25% (98), 22% (99)) or H<sub>3</sub>PO<sub>4</sub> (100); note that the isomeric benzaldehyde diphenylacetal is unreported. For formn. of resin from  $\bar{C}$  with phenol see (101).]

( $\bar{C}$  with 2 moles  $\beta$ -naphthol (1:1540) on htg. condenses with loss of  $HCl + H_2O$  giving (97% yield (102)) (103) 9-phenyl-1,2,7,8-dibenzoxanthene [Beil. XVII-98], pr. or tbs. from  $AcOH$ , m.p. 190–191° (103), 190° (102); this prod. is also obtd. from benzaldehyde (1:0195) by condensation with  $\beta$ -naphthol in  $AcOH$  in s.t. at 200° for 2 days (104) or in pres. of  $H_2SO_4$  (104) at 100°; see also under benzaldehyde (1:0195) for use as test for latter.]

$\bar{C}$  with amines ( $\bar{C}$  with aniline (2 moles) in pres. of  $Zn$  dust (92) or  $BeCl_2$  at 120–125° for 2 hrs. (91) condenses giving (54% yield (91)) 4,4'-diamino-triphenylmethane [Beil. XIII-274, XIII-1-(89)], cryst. from  $C_6H_6$  with 1 mole solvent, m.p. 106° (106), 104–105° (92), cryst. from dry ether without solvent, m.p. 139–140° (106), 139° (107) (corresp. diacetyl deriv., m.p. 233–234° (108) (109)); this compound is also obtd. from benzaldehyde (1:0195) by condensation with 2 moles aniline in various ways, e.g., see (108) (106) (107).]

( $\bar{C}$  with  $N,N$ -dimethylaniline (2 moles) in pres. of  $ZnCl_2$  at 100° (110) condenses giving 4,4'-bis-(dimethylamino)-triphenylmethane (leuco-Malachite Green) [Beil. XIII-275, XIII-1-(89)], cryst. from  $C_6H_6$  or alc. in 3 forms, m.p. 102° (111) (112), m.p. 93–94° (111), 92–93° (112), and 77° (112) cf. (111); this prod. is also obtd. from benzaldehyde (1:0195) by condensation with 2 moles  $N,N$ -dimethylaniline in various ways, e.g., with  $ZnCl_2$  at 100° (113) (112), or with  $POCl_3$  (alm. 100% yield (114)) ]

[For study of reactivity of  $\bar{C}$  toward pyridine or piperidine see (115).]

$\bar{C}$  with other nitrogenous reactants ( $\bar{C}$  (excess) with thiourea at not above 150° gives (116) (117) a salt,  $C_6H_5N_2S_2HCl$ , m.p. 236° (117), regarded as 4,6-di-imino-2-phenyl-1,3,5-dithiazane (117). — For analogous behavior of  $\bar{C}$  with  $N$ -phenylthiourea and with  $N$ -( $p$ -tolyl)-thiourea see (117) ]

( $\bar{C}$  with  $Zn$  salt of  $o$ -aminophenyl mercaptan in  $AcOH/NaOAc$  refluxed 30 min. in current of  $H_2S$  gives (low yield (118)) 2-phenylbenzothiazole, m.p. 114° cor.)

$\bar{C}$  with organometallic reactants ( $\bar{C}$  with  $MeMgI$  gives (22% yield (119))  $\alpha$ -stilbene dichloride (3:4854) + ethane but no isopropylbenzene (cumene) or *sym*-dimethyldiphenylethane; however,  $\bar{C}$  with  $MeMgCl$  gives (120) no  $\alpha$ -stilbene dichloride but instead a mixture of four other compds., viz., isopropylbenzene (cumene) (1:7440), 1-chloro-1,2-diphenylpropane, and two forms of 2,4-diphenylbutane.)

( $\bar{C}$  with  $C_6H_5MgBr$  gives (119) cf. (121) triphenylmethane (1:7220) +  $\alpha$ -stilbene dichloride (3:4854) + biphenyl (1:7175) ]

( $\bar{C}$  with  $Me_2Zn$  gives (122) isopropylbenzene (cumene) (1:7440).]

( $\bar{C}$  does not react with  $Hg$  di- $p$ -tolyl even on refluxing in toluene for 300 hrs (123).]

⑤ Hydrolysis to benzaldehyde:  $\bar{C}$  on boilg. with 10%  $K_2CO_3$  soln. gives benzaldehyde (1:0195); after acidification with  $HCl$  the benzaldehyde may be detected with fuchsin aldehyde reagent. (Dif. from pure benzyl chloride (3:6335) or pure benzotrichloride (3:6540).)

⑥ Benzaldehyde phenylhydrazone: m.p. 156° u.c. (From  $\bar{C}$  with 3 moles phenylhydrazine refluxed in alc. for 2 hrs. (55% yield (124)); note that from the mother liquor small amounts of an isomeric ( $\gamma$ ) benzaldehyde phenylhydrazone, m.p. 154–155°, are obtd. (124).]

⑦ Benzaldehyde semicarbazone: m.p. 219–220° u.c. (124). [From  $\bar{C}$  (3.2 g.) with semicarbazide hydrochloride (4.4 g.) +  $Na_2CO_3$  (2.1 g.) refluxed a few hrs. in alc. and the ppt. recrystd. from hot sq. (124); note that the m.p. of this prod. varies somewhat with rate of htg. cf. (1:0195).]

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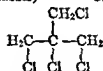
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3:6335 1,2,3-TRICHLORO-2(CHLOROMETHYL)  
PROPANE



Beil. I —



I<sub>1</sub>—

I<sub>2</sub>-(89)

B.P. 206-210° cor. (1)  
87° at 9 mm. (2)

$D_4^{25} = 1.481$  (1)

$n_D^{20} = 1.508$  (1)

Colorless odorless oil (2).

[For formn. of  $\bar{C}$  (together with other products) from *ter*-butyl chloride (3:7045) +  $\text{Cl}_2$  see (1); from 3-chloro-2-(chloromethyl)propene-1 (3:5633) in  $\text{CHCl}_3$  by shaking with  $\text{Cl}_2/\text{aq.}$  see (2).]

3:6335 (1) Rogers, Nelson, *J. Am. Chem. Soc.* 58, 1028 (1936). (2) Kleinfeller, *Ber.* 62, 1595 (1929).

— 1,3,5-TRICHLOROBENZENE



Beil. V - 204

V<sub>1</sub>-(113)

V<sub>2</sub>-(156)

B.P. 208°

M.P. 63°

See 3:1400. Division A: Solids.

3:6345 2,3-DICHLOROTOLUENE



Beil. V - 295

V<sub>1</sub>—

V<sub>2</sub>—

B.P. 207-208° at 760 mm. (1)  
204-206° at 755 mm. (2)  
61-62° at 3 mm. (8)

$n_D^{20} = 1.5511$  (8)

[For prepn. of  $\bar{C}$  from 2-chloro-3-aminotoluene [Beil. XII-870, XII<sub>1</sub>-(404)] via diazotization and use of  $Cu_2Cl_2$  reaction (alm. quant. yield (2), 64% (8)) see indic. refs.; for formn. of  $\bar{C}$  (together with other dichlorotoluenes) from toluene or *o*-chlorotoluene (3:8245) with  $Cl_2$  in pres. of  $FeCl_3$  or  $MoCl_5$  see (3) (4), from *o*-chlorotoluene +  $Cl_2$  +  $Al/Hg$  see (4).]

[ $\bar{C}$  with  $Cl_2$  in pres. of  $Al/Hg$  gives (70% yield (5)) 2,3,4-trichlorotoluene (3:0425), m.p. 41°.] [ $\bar{C}$  with  $Br_2$  at 180–200° gives (8) 2,3-dichlorobenzal (di)bromide (not isolated) which on hydrolysis with conc.  $H_2SO_4$  gives (71% yield (8)) 2,3-dichlorobenzaldehyde (3:1480).]

$\bar{C}$  on mononitration with conc.  $HNO_3$  (6) or cold mixt. of 2 pts. conc.  $HNO_3$  + 3 pts. conc.  $H_2SO_4$  (2) yields 2,3-dichloro-4-nitrotoluene [Beil. V-332], ndls. from alc. +  $AcOH$ , m.p. 50.5–51.5° (2), 51° (6);  $\bar{C}$  on dinitration with mixt. of 7 pts. fuming  $HNO_3$  + 3.5 pts. conc.  $H_2SO_4$  yields (2) 2,3-dichloro-4,6-dinitrotoluene [Beil. V-345], cryst. from  $AcOH$  or alc., m.p. 71–72° (2).

$\bar{C}$  on oxidn. with alk.  $KMnO_4$  (6) or with dil.  $HNO_3$  for some hrs. in s.t. at 140° (2) (6) yields 2,3-dichlorobenzoic acid (3:4650), m.p. 166° (6), 163° (2).

$\bar{C}$  on sulfonation with 2 pts. 10% oleum at 50° gives (7) mixt. of 89% 2,3-dichlorotoluene-sulfonic acid-6 (corresp. sulfonyl chloride, m.p. 51–52° (7), corresp. sulfonamide, m.p. 228° (7)) and 11% 2,3-dichlorotoluenesulfonic acid-5 (corresp. sulfonyl chloride, m.p. 87° (7), corresp. sulfonamide, m.p. 185° (7)).

3:6345 (1) Wynne, Greeves, *Proc. Chem. Soc.* **11**, 151 (1895). (2) Cohen, Dakin, *J. Chem. Soc.* **79**, 1128–1129 (1901). (3) Seelig, *Ann.* **237**, 157, 166 (1887). (4) Ref. 2, pp. 1114–1117. (5) Cohen, Dakin, *J. Chem. Soc.* **81**, 1339–1340 (1902). (6) Ref. 3, pp. 162–163 (7) Silvester, Wynne, *J. Chem. Soc.* **1936**, 692–694. (8) Marvel, Overberger, Allen, Johnston, Saunders, Young, *J. Am. Chem. Soc.* **68**, 861–862 (1946).

### 3:6355 3,4-DICHLOROTOLUENE


 $C_7H_5Cl_2$ 

Beil. V - 290  
V<sub>1</sub>-(152)  
V<sub>2</sub>-

B.P.

F.P.

207–208.1° cor. at 770 mm. (1)	–16.0° (1)	$D_{20}^{20} = 1.2541$ (1)
208.3–208.8° at 745.5 mm. (2)	.	1.2512 (4)
205.5–206.5° (3)		$n_D^{22} = 1.5490$ (1)
200.5° u.c. at 741 mm. (4)		

For f.p./compn. diagram of system:  $\bar{C}$  + 2,4-dichlorotoluene (3:6290) see (1); the eutectic conts 52%  $\bar{C}$  and freezes about –38° (1).

[For prepn. of  $\bar{C}$  from 4-chloro-3-aminotoluene [Beil. XII-871, XII<sub>1</sub>-(404)] by diazotization and  $Cu_2Cl_2$  reactn. (77% yield (5)) see (5) (6); similarly from 3-chloro-4-aminotoluene [Beil. XII-989, XII<sub>1</sub>-(436)] see (4) (3) (1); from 2-chloro-4-methylphenol (3:6215) with  $PCl_5$  see (7); from salts of 3,4-dichlorotoluenesulfonic acid-2 or 3,4-dichlorosulfonic acid-5 by hydrolysis see (8).]

[For formn. of  $\bar{C}$  (42% together with 58% 2,4-dichlorotoluene (3:6290)) from *p*-chlorotoluene (3:8287) with  $Cl_2$  in pres. of  $Fe$  see (1); for formn. of  $\bar{C}$  (together with other isomers) from toluene with  $Cl_2$  in pres. of  $I_2$  (9) (10) or of  $MoCl_5$  (11) (12) or with  $SO_2Cl_2$  at 160° (13) see indic. refs.; for formn. of  $\bar{C}$  (together with other isomers) from *m*-chlorotoluene (3:8275) or *p*-chlorotoluene (3:8287) with  $Cl_2$  in pres. of  $Al/Hg$  see (14).]

[ $\bar{C}$  with  $Cl_2$  in pres. of  $Al/Hg$  yields exclusively (15) 2,4,5-trichlorotoluene (3:2100), m.p. 81–82° (15);  $\bar{C}$  at its b.p. treated with  $Cl_2$  yields (16) (5) (17) 3,4-dichlorobenzal dichloride (3:6876), b.p. 257°.

$\bar{C}$  on mononitration with mixt. of 2 pts. conc.  $\text{HNO}_3$  + 4 pts. conc.  $\text{H}_2\text{SO}_4$  yields (6) (18) 3,4-dichloro-6-nitrotoluene [Beil. V-331], ndls. from alc. +  $\text{AcOH}$ , m.p. 63-64° (6) (19), 63° (20);  $\bar{C}$  on dinitration yields (6) 3,4-dichloro-2,6-dinitrotoluene [Beil. V-345], ndls. from  $\text{AcOH}$ , m.p. 91.5-92.5° (6) (19).

$\bar{C}$  on oxidn. (2) with  $\text{CrO}_3$  (9) (10), with  $\text{KMnO}_4$  (21), or with dil.  $\text{HNO}_3$  in a.t. at 130-150° (4) (6) (8) yields 3,4-dichlorobenzoic acid (3:4925), m.p. 206°.

$\bar{C}$  on sulfonation with fuming  $\text{H}_2\text{SO}_4$  yields (6) 3,4-dichlorotoluenesulfonic acid-6 (corresp. sulfonyl chloride, m.p. 81° (6), 82° (22), corresp. sulfonamide, m.p. 190-191° (6), 189° (22)); note, however, that the isomeric derivs., viz., 3,4-dichlorotoluenesulfonyl chloride-2, m.p. 49° (8), and 3,4-dichlorotoluenesulfonamide, m.p. 186° (8), have been independently prep'd.]

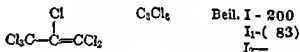
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### 3:6370 HEXACHLOROPROPENE



B.P.

209-210° at 760 mm. (1) (2)

122-123° at 50 mm. (1)

99° at 15 mm. (2)

$D_4^{20} = 1.7652$  (1)  $n_D^{20} = 1.5091$  (1)

Oil with fragrant odor. — Insoluble aq.

[For prepn. of  $\bar{C}$  from *sym.*-heptachloropropane (3:6860) by loss of  $\text{HCl}$  in presence of  $\text{AlCl}_3$  in  $\text{CCl}_4$  at 60-70° (83% yield) see (3); from *asym.*-heptachloropropane (3:0200) by htg. at 250-420°, especially in presence of  $\text{ZnCl}_2$  or  $\text{CuCl}$  (4) (with latter tetrachloroethylene (3:5460), is also formed (4) (5)), or by htg. with alc.  $\text{KOH}$  at 50-60° (90% yield (6) (1); from heptachloro-*n*-butyraldehyde [Beil. I-(346)] by actn. of 2 moles  $\text{NaOEt}$  see (7).]

$\bar{C}$  with  $\text{AlCl}_3$  + 1 mole trichloroethylene (3:5170) in  $\text{CH}_2\text{Cl}_2$  (3:5020) or  $\text{CHCl}_3$  (3:5050) at 30-37° gives (82% yield (6)) 1,1,2,3,3,4,5,5,5-nonachloropentene-1, colorless liq. with cedar-like odor, b.p. 128° nt 2-3 mm., 86° at 0.2 mm.,  $D_4^{20} = 1.812$ ,  $n_D^{20} = 1.5703$  (6); with excess trichloroethylene (3:5170) prod. is mixt. consisting exclusively of two dodecachloroheptenes,  $\text{C}_{12}\text{H}_2\text{Cl}_{12}$ , one m.p. 94-96°, the other, m.p. 58-62° (6).

$\bar{C}$  with  $\text{AlCl}_3$  + 1,2-dichloroethylene (3:5030) in  $\text{CH}_2\text{Cl}_2$  soln. yields (8) a single 1,1,2,3-, 113-113.5° at 2 mm.,  $D_{21}^{20} = 1.749$ , (80% yield (8)) a mixt. of penta-

$\bar{C}$  forms with  $\text{AlCl}_3$  at 80° a yel. cryst. addn.-prod. sparingly sol. in  $\text{CCl}_4$  but regenerating  $\bar{C}$  upon treatment with aq. (8).

$\bar{C}$  on cautious warming with conc.  $\text{H}_2\text{SO}_4$  (9) (10) (2) (11) or on boilg. with an aqueous suspension of  $\text{BaCO}_3$  (2) yields  $\alpha,\beta,\beta$ -trichloroacrylic acid (3:1840) spar. sol. cold aq., eas. sol. hot aq., pr. from  $\text{CS}_2$ , m.p. 76° (2).



$\bar{C}$  does not add  $Br_2$  (10), but  $\bar{C}$  in sunlight adds  $Cl_2$  yielding (10) octachloropropane (3:4450) q.v.

$\bar{C}$  with alc. NaOEt yields (1) triethyl *ortho*- $\alpha,\beta,\beta$ -trichloroacrylate, b.p. 236-237°,  $D_4^{20} = 1.2183$ ,  $n_D^{20} = 1.4649$  (1). [This *ortho* ester on htg. with 2 vols. conc. HCl yields (1) ethyl  $\alpha,\beta,\beta$ -trichloroacrylate, b.p. 192-194°,  $D_4^{20} = 1.3740$ ,  $n_D^{20} = 1.4839$  (1), which can be hydrolyzed by conventional methods to  $\alpha,\beta,\beta$ -trichloroacrylic acid (see above).]

3:6370 (1) Fritsch, *Ann.* 297, 314-316 (1897). (2) Böseken, Dujardin, *Rec. trav. chim.* 32, 98-100 (1913). (3) Prins, *Rec. trav. chim.* 34, 231-232 (1935). (4) Böseken, van der Scheer, de Voogt, *Rec. trav. chim.* 34, 78-93 (1915). (5) Böseken, *Rec. trav. chim.* 43, 467-468 (1915). (6) Böseken, *Rec. trav. chim.* 52, 663-664 (1927). (7) Böseken, Schimmel, *Rec. trav. chim.* 32, 152 (1913). (8) Prins, *Ger.* 261,689, July 2, 1913; 6 (1914).

3:6373 DI(TRICHLOROVINYL) ETHER  $\begin{array}{c} Cl \quad Cl \quad C_6OCl_2 \\ | \quad | \\ Cl_2C=C-O-C=CCl_2 \end{array}$  Beil. I - 725  
I<sub>1</sub>-  
I<sub>2</sub>-

B.P. 210° (1)  $D_4^{21} = 1.654$  (1)

[For prepn. of  $\bar{C}$  from decachlorodiethyl ether (3:1676) by treatment with alc. K<sub>2</sub>S see (1).]

$\bar{C}$  with  $Cl_2$  in sunlight adds 2 moles halogen yielding (1) decachlorodiethyl ether (3:1676), m.p. 69°.

$\bar{C}$  with  $Br_2$  in sunlight adds 2 moles halogen yielding (1) bis-( $\alpha,\beta$ -dibromo- $\alpha,\beta,\beta$ -trichloroethyl) ether, m.p. 96° (1).

3:6373 (1) Malaguti, *Ann. chim.* (3) 16, 19-23 (1846).

3:6375 ETHYL  $\gamma$ -CHLOROACETOACETATE  $\begin{array}{c} C_6H_9O_3Cl \\ CH_2-C-CH_2-C=O \\ | \quad || \quad | \\ Cl \quad O \quad OEt \end{array}$  Beil. III - 663  
(Ethyl  $\gamma$ -chloro- $\beta$ -keto-*n*-butyrate) III<sub>1</sub>-(233)  
III<sub>2</sub>-(426)

B.P.		F.P.			
210° dec.	(1)	-5° (2) (9)	$D_4^{20} = 1.2157$	(4)	
205° dec.	(2) (9)	-8° (1)	$D_4^{17} = 1.2176$	(4)	$n_D^{17} = 1.4546$ (4)
117-119° at 17 mm.	(3)				1.45452 (1)
107° at 14 mm.	(4)				
105° at 11 mm.	(2) (9)				
102° at 12 mm.	(1)		$D_4^{15} = 1.2182$	(4)	
103° at 12 mm.	(19)				
92-93° at 6 mm.	(19)				
80° at 3 mm.	(19)				

[See also ethyl  $\alpha$ -chloroacetoacetate (3:6207).]

Colorless limpid liq. which soon turns yellow (4). — Almost insol. aq. but miscible with most org. solvents. — [Note that purity of material of earlier workers (5) has been seriously questioned (2).]

[For prepn. of  $\bar{C}$  from acetylketene (ketene dimer (6) (7)) by conversion with  $Cl_2$  to  $\gamma$ -chloroacetoacetyl chloride (3:9088) and reactn. of the latter with excess alc. EtOH at 0° see (3); from ethyl chloroacetate (3:5700) (2 moles) with Mg (1 mole) in dry ether contg.  $HgCl_2$  (56% yield (1)) cf. (19) or with Mg in dry ether contg.  $I_2$  (35% yield (4)) or with

Al/Hg in pres. of a trace of EtOH (8) see indic. refs.; from chloroacetaldehyde (3:7212) with ethyl diazoacetate see (5); from ethyl  $\gamma$ -chloro- $\beta$ -hydroxy- $n$ -butyrate [Beil. III-310, III-116] by careful oxidn. with  $K_2Cr_2O_7 + H_2SO_4$  (poor yield) see (9).]

$\bar{C}$  on hydrolysis with aq. HCl for 3 hrs undergoes ketonic splitting yielding (1) chloroacetone (3:5425) +  $CO_2$  + EtOH (note that this does not distinguish  $\bar{C}$  from ethyl  $\alpha$ -chloroacetoacetate which yields same products).

[ $\bar{C}$  with alc. NaOEt at  $100^\circ$  undergoes bimolecular condensation with loss of 2 HCl yielding (10) diethyl succinylsuccinate [Beil. X-894, XI-434], m.p.  $125-126^\circ$  (10); this same condensation is also effected by other alkaline agents, e.g., sodium phenolate, dil. aq. NaOH,  $NH_4OH$ ,  $NH_3$  in ether, KOAc alone or in pres. of alc. or  $C_6H_6$ , diethyl sodiomalonate or  $Me_2NH$  in  $C_6H_6$ , or K phthalimide (10).]

[ $\bar{C}$  with ethyl orthoformate (1:3241) in  $Ac_2O$  refluxed for  $\frac{1}{2}$  hr. ppts. on cooling (45% yield (11)) ethyl  $\gamma$ -chloro- $\alpha$ -ethoxymethylene-acetoacetate, colorless ndls. from alc. or  $C_6H_6$ , m.p.  $98^\circ$  (11).]

Note that  $\bar{C}$  is capable of displaying keto-enol tautomerism as is shown by the following reactions:

$\bar{C}$  with  $FeCl_3$  soln. gives red coloration (1) (4) (9) (19);  $\bar{C}$  conts. 10.9% enol, but 4% soln. of  $\bar{C}$  in ether conts. 53% enol. (19).

$\bar{C}$  forms a series of metallic salts of the enolic form; these are in general insol. in aq. but soluble in org. solvents: e.g.,  $Cu(C_6H_5O_3Cl)_2$  (from  $\bar{C}$  on shaking with aq.  $Cu(OAc)_2$ ), green ndls. from  $C_6H_6$ , m.p.  $163-169^\circ$  dec. (9) (4) cf. (19),  $167.5^\circ$  dec. (1),  $163^\circ$  (8);  $Mg(C_6H_5O_3Cl)_2$  (from  $\bar{C}$  shaken with aq.  $MgSO_4 + NH_4Cl$ ), m.p.  $170^\circ$  (1);  $Zn(C_6H_5O_3Cl)_2$  (from  $\bar{C}$  on shaking with  $NH_4OH/ZnSO_4$ ), m.p.  $121^\circ$  (1);  $Ni(C_6H_5O_3Cl)_2$  (from  $\bar{C}$  on shaking with  $Ni(OAc)_2 + NH_4OH$ ), m.p.  $131-132^\circ$  (1); other metals behave similarly (1).

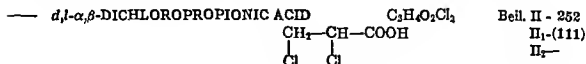
$\bar{C}$  couples with diazonium salt solns. in pres. of NaOAc yielding the corresp.  $\alpha$ -(arylhydrazines) of ethyl  $\gamma$ -chloro- $\alpha,\beta$ -diketo- $n$ -butyrate (ethyl  $\gamma$ -chloro- $\alpha$ -(aryldiazo)acetoacetates (cf. dif. behavior of isomeric ethyl  $\alpha$ -chloroacetoacetate (3:6207)): e.g.,  $\bar{C}$  with benzenediazonium chloride soln. in pres. of NaOAc at  $0^\circ$  gives (12) (13) ethyl  $\gamma$ -chloro- $\beta$ -keto- $\alpha$ -phenylhydrazono- $n$ -butyrate, sparing sol. yel. ndls. from alc., m.p.  $92-93^\circ$  (12) (13),  $92^\circ$  (14) (note that this prod. on htg. with alc. KOAc loses HCl and ring-closes to 3-carbethoxy-4-hydroxy-1-phenylpyrazole, colorless pr. from alc., m.p.  $85^\circ$  (14) (15)); similarly  $\bar{C}$  with  $p$ -nitrobenzenediazonium chloride soln. in pres. of NaOAc at  $0^\circ$  gives (16) ethyl  $\gamma$ -chloro- $\alpha$ -( $p$ -nitrobenzeneazo)acetoacetate, yel. ndls. from alc., m.p.  $135^\circ$  (16) (note that this prod. with hot alc. KOAc loses HCl and ring-closes to 3-carbethoxy-4-hydroxy-1-( $p$ -nitro)phenylpyrazole, colorless ndls. from AcOH, m.p.  $220^\circ$  (16). — [For analogous reactions of  $\bar{C}$  with numerous other diazonium salts see the papers represented by (16) (14) (17).]

$\bar{C}$  with thiourea on warming in alc. for 4 hrs. loses HCl and ring-closes yielding (9) ethyl (2-aminothiazolyl-4)acetate, colorless cryst. from  $C_6H_6$ , m.p.  $94^\circ$  (18),  $74^\circ$  (9) (one of these is probably a misprint for the other).

3:6375 (1) Hamel, *Bull. soc. chim.* (4) 29, 390-402 (1921). (2) Lespieau, *Bull. soc. chim.* (4) 9, 31-33 (1911). (3) Hurd, Abernathy, *J. Am. Chem. Soc.* 62, 1147-1148 (1940). (4) Alexandrow, *Ber.* 46, 1021-1024 (1913). (5) Schlotterbeck, *Ber.* 42, 2570-2571 (1909). (6) Boese, *Ind. Eng. Chem.* 32, 16-22 (1940). (7) Hurd, Williams, *J. Am. Chem. Soc.* 58, 962-968 (1936). (8) Picha, Dohrt, *Weiss, Monatsch.* 27, 1245-1249 (1906). (9) Lespieau, *Bull. soc. chim.* (3) 33, 463-464 (1905); *Compt. rend.* 138, 422 (1904). (10) Sommelet, Couroux, *Bull. soc. chim.* (4) 29, 402-406 (1921).

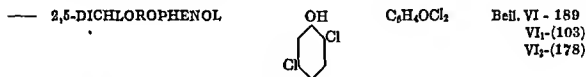
(11) Benary, Ebert, *Ber.* 56, 1897-1898 (1923). (12) Favrel, *Compt. rend.* 145, 196 (1907). (13) Favrel, Prevost, *Bull. soc. chim.* (4) 43, 245-246 (1931). (14) Chattaway, *Lye, Proc. Roy. Soc. London A-137*, 492, 497, 501 (1932). (15) Wolf, *Ann.* 313, 15 (1900). (16) Chattaway, Ashworth, *J. Chem. Soc.* 1933, 1146. (17) Chattaway, *Lye, Proc. Roy. Soc. London A-135*,

294-295 (1932). (18) Steude, *Ann.* 261, 30-31 (1891). (19) Arndt, Loewe, Capuano, *Rev. faculté sci. univ. Istanbul* 8-A, 122-152 (1943); *C.A.* 39, 1626 (1945).



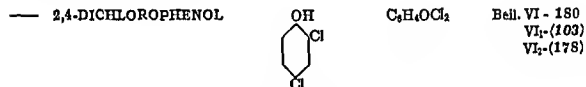
B.P. M.P.  
 210° sl. dec. at 762 mm. 49-50°

See 3:0855. Division A: Solids.



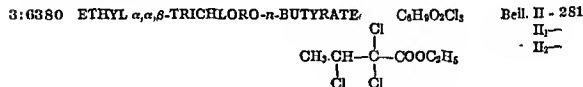
B.P. 211° at 744 mm. M.P. 58°

See 3:1190. Division A: Solids.



B.P. 211° M.P. 45°  $D_{25}^{25} = 1.4723$   $n_D^{25} = 1.1720$

See 3:0560. Division A: Solids.



B.P. 212° (1)  $D_{25}^{25} = 1.3094$  (2)  
 174.2° cor. at 250 mm. (2)  $D_{20}^{20} = 1.3138$  (2)  
 101.5° at 17 mm. (3)  $D_{15}^{15} = 1.3183$  (2)

[For prepn. of  $\bar{C}$  from  $\alpha,\alpha,\beta$ -trichloro-*n*-butyric acid (3:1280) in EtOH with 10% conc.  $H_2SO_4$  in s.t. at 100° for 3 days see (2); note that the acid esterifies with difficulty and attempts to use the dry HCl method give only very poor yields (2).]

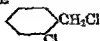
$\bar{C}$  with Zn dust in moist ether loses HCl giving (almost 100% yield (3)) ethyl  $\alpha$ -chloro-crotonate (3:8523).

3:6380 (1) Judson, *Ber.* 3, 787 (1870). (2) Perkin, *J. Chem. Soc.* 65, 424 (1894). (3) Michael, Schulthess, *J. prakt. Chem.* (2) 43, 504-596 (1891).

## 3:6400 o-CHLOROBENZYL CHLORIDE

 $C_7H_6Cl_2$ 

Boil. V - 297

V<sub>1</sub>-(152)V<sub>2</sub>-(231)

B.P. 213-214°	(1)
105-107°	at 28 mm. (2)
109.0-109.2°	at 25.6 mm. (3)
110°	at 24 mm. (4)
94°	at 15 mm. (5)
96-98°	at 14 mm. (4)
94-95°	at 10 mm. (6)
84-85°	at 3 mm. (4)

(For prepn. of  $\bar{C}$  from o-chlorobenzyl alcohol [Beil. VI-444, VI<sub>1</sub>-(222)] with  $PCl_5$  (7) or with  $SOCl_2$  + pyridine (5) see indic. refs.; from o-chlorotoluene (3:8245) with  $PbCl_4$ - $2NH_4Cl$  (1) or with  $Cl_2$  (8) (9) in ultra-violet light (4) see indic. refs.; from benzyl chloride (3:8535) with  $Cl_2$  see (10).]

[For condens. of  $\bar{C}$  with p-chlorophenol and use of prod. as anti-moth prepn. see (11); for use in prepn. of condensation prod. with sulfonated phenol see (12).]

[ $\bar{C}$  with phenol in toluene yields (13) 2-(o-chlorobenzyl)phenol, b.p. 146-151° at 3 mm. (benzoate, b.p. 173-176° at 2.5 mm.), and o-chlorobenzyl phenyl ether, b.p. 140-145° at 2.5 mm.,  $\bar{C}$  with 2,4-dichlorophenol (3:0560) in toluene yields 2-(o-chlorobenzyl)-4,6-dichlorophenol, m.p. 59.5-60.6° (benzoate, m.p. 81-82°), and o-chlorobenzyl 2,4-dichlorophenyl ether, m.p. 61-62°.]

[ $\bar{C}$  with phenol +  $AlCl_3$  yields (13) 4-(o-chlorobenzyl)phenol, m.p. 68-69° (benzoate, m.p. 64.5-65.5°), and 2-(o-chlorobenzyl)phenol (see above);  $\bar{C}$  with 2,6-dichlorophenol (3:1395) +  $AlCl_3$  yields (13) 4-(o-chlorobenzyl)-2,6-dichlorophenol, m.p. 86.5-87.5° (benzoate, m.p. 86-87°).]

[ $\bar{C}$  with Mg in 10 moles dry ether gives (60-75% yield (4)) cf. (25) o-Cl.C<sub>6</sub>H<sub>4</sub>.CH<sub>2</sub>MgCl (particularly sensitive to air oxidn.); this with  $CO_2$  followed by acidification or with methyl chloroformate (3:5075) followed by hydrolysis yields (4) o-chlorophenylacetic acid, m.p. 94-95° (3:2040); the R.MgCl cpd. with phenyl isocyanate as directed (22) for p-isomer should yield o-chlorophenylacetanilide [Beil. XII-275], m.p. 140° cor. (23), 133.5° (24), although this method has not been specifically reported for  $\bar{C}$ ; the RMgCl cpd. with  $HgCl_2$  gives (25) o-chlorobenzyl  $HgCl$ , m.p. 111°, or with  $HgBr_2$  gives (25) o-chlorobenzyl  $HgBr$ , m.p. 128°.]

[For study of behavior of  $\bar{C}$  with NaOEt see (14) (7); for study of rate of reaction of  $\bar{C}$  with LiI, NaI, or KI (6) (5) or with  $Na_2SO_3$  (2) see indic. refs., for study of acid hydrolysis of  $\bar{C}$  in various solvents see (5); for reaction of  $\bar{C}$  with KCN yielding o-chlorobenzyl cyanide (which on hydrolysis gives o-chlorophenylacetic acid (3:2040)) see (15) (16); for behavior of  $\bar{C}$  with cellulose (17) or sodium cellulose (18) see indic. refs.]

$\bar{C}$  refluxed 4 hrs. with hexamethylenetetramine (1 mole) in 60% alc. soln. yields (19) o-chlorobenzaldehyde (3:6410) q.v.;  $\bar{C}$  htd. in xylene with p-nitrophenylhydrazine yields (20) o-chlorobenzal-p-nitrophenylhydrazone, m.p. 241° (20).

$\bar{C}$  on mononitration with 1.2 pts. fuming  $HNO_3$  at 30-40° gives (35% yield (21)) 2-chloro-5-nitrobenzyl chloride, pr. from alc., m.p. 66° (21).

3:6400 (1) Seyewitz, Trautwitz, *Compt. rend.* 136, 241 (1903). (2) Sprang, *J. Am. Chem. Soc.* 52, 1640-1649 (1930). (3) de Bruyne, Davis, *Groes, J. Am. Chem. Soc.* 55, 3938 (1933). (4) Austin, Johnson, *J. Am. Chem. Soc.* 54, 657 (1932). (5) Bennett, Jones, *J. Chem. Soc.* 1933, 1818. (6) Conant, Hussey, *J. Am. Chem. Soc.* 47, 456 (1925). (7) Olivier, *Rec. trav. chim.* 41, 308-309 (1921). (8) Jones, *J. Chem. Soc.* 1933, 1839. (9) Zelinsky & Schering-Kahlbaum, *Ger.* 478,084, June 20, 1929; *Cent.* 1929, II 1216. (10) Olivier, *Rec. trav. chim.* 41, 419-421 (1921).

(11) *J. Biol. Chem.* 58, 220 (1923). (10) Mehner, *J. prakt. Chem.* (2) 62, 551-555 (1900). (17) Niethammer, König, *Cellulosechem.* 19, 201-205 (1920). (18) Ball, Hilbert, *Can. J. Research* 7, 481-498 (1932). (19) Mayer, English, *Ann.* 417, 78 (1918). (20) Busch, Lang, *J. prakt. Chem.* (2) 144, 312 (1930).  
(21) Melsenheimer, Zimmermann, von Kummer, *Ann.* 440, 225-226 (1920). (22) Underwood, Gale, *J. Am. Chem. Soc.* 59, 2117-2119 (1934). (23) Jenkins, Richardson, *J. Am. Chem. Soc.* 55, 1619 (1933). (24) Mehner, *J. prakt. Chem.* (2) 62, 558 (1900). (25) Ware, Hixon, *J. Am. Chem. Soc.* 60, 1262-1263 (1938).

## 3:6410 o-CHLORO BENZALDEHYDE

 $C_7H_5OCl$ 

Bell. VII - 233  
VII<sub>1</sub> - (132)

B.P.		M.P.	
213-214°	(1)	11° (4)	$D_4^{20} = 1.2512$ (6) $n_D^{20} = 1.50708$ (6)
	(2)	(14)	
209.7-211.7° at 760 mm.	(3)		
208° at 748 mm.	(4)		
205-206° cor. at 740 mm.	(5)		
96.0-96.0° at 16 mm.	(3)		

Oil, volatile with steam. —  $\bar{C}$  often contains o-benzyl chloride (3:6400) as impurity (7). —  $\bar{C}$  very easily oxidized in air (probably also of variant constants). —  $\bar{C}$  yields  $\text{NaHSO}_3$  epd. (15) (21).

[For prepn. of **6** from *o*-chlorotoluene (**3:8**)<sup>(245)</sup> with MnO<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub> (**8**), or PbO<sub>2</sub> (24% yield) (**21**), or CrO<sub>2</sub>Cl<sub>2</sub> in CCl<sub>4</sub> (**9**) or CS<sub>2</sub> (**10**), or via halogenation to *o*-chlorobenzal (di)chloride (**3:6626**) (**5**) (**12**) or *o*-chlorobenzal (di)bromide (**11**) and subsequent hydrolysis with fuming H<sub>2</sub>SO<sub>4</sub> (**11**) (**12**) (**1**) or anhydrous oxalic ac. (**14**) see indicated refs.; for prepn. from *o*-nitrobenzaldehyde via *o*-aminobenzaldehyde see (**12**); from *o*-chlorobenzyl alc. by dehydrogenation with CuO + dinitrobenzene in quinoline (86% yield) see (**13**); from *o*-chlorobenzyl chloride (**3:0400**) . . . . . chlorido (**3:6040**) by cat. reduct.

$\text{C}$  with  $\text{CrO}_3$  (16) or  $\text{KMnO}_4$  (2) oxidizes to *o*-chlorobenzoic acid (3:4150), m.p. 141°. [For study of auto-oxidn. see (17).] —  $\text{C}$  on cat. hydrogenation gives (yield: 90% (18); 50% (16)) *o*-chlorobenzyl alc., m.p. 60° (16), 64–65° (18). —  $\text{C}$  with conc. alk. undergoes Cannizzaro reactn. (for study on dioxane soln. see (20)) although presumable products, *o*-chlorobenzyl alc. and *o*-chlorobenzoic alc., have not (by this reactn.) actually been isolated.

$\bar{C}$  with dil. alc. KCN for 4 hrs. at  $00^\circ$  gives (21% yield (22)) 2,2'-dichlorobenzoin, m.p.  $63-64^\circ$  (22). —  $\bar{C}$  with KCN + HCl yields *o*-chloromandelonitrile which on hydrolysis with HCl gives *o*-chloromandelic acid, m.p.  $84-85^\circ$  (23).

with  $\text{HCl}$  gives *o*-chloromandelic acid, m.p. 84–85° (23).  
 $\dot{\text{C}}$  on hgt. with  $\text{NaOAc} + \text{Ac}_2\text{O}$  for 8 hrs. at 180–200° undergoes Perkin reactn. giving (71% yield (12)) *o*-chlorocinnamic acid, m.p. 214° (12). [This with  $\text{Br}_2$  in  $\text{CHCl}_3$  gives (24) *o*-chlorocinnamic acid dibromide, m.p. 183° (24).] —  $\dot{\text{C}}$  + malonic acid + pyridine gives (38) alm. quant. yield of *o*-chlorocinnamic ac., m.p. 211–212° (31). [In absence of pyridine reactn. gives 63% yield *o*-chlorobenzalmalonic acid, m.p. 102° (37).]

C on mononitration as specified (25) gives 2-chloro-5-nitrobenzaldehyde, *cryst. from*

dil. AcOH, m.p. 78–79° (25), 80° (26). [Oxime, m.p. 147–148° (26); corresp. acid, 2-chloro-5-nitrobenzoic acid, m.p. 165° (25).]

$\bar{C}$  in alc. warmed at 58–60° for 2 hrs. with  $(NH_4)_2CO_3 + KCN$  as directed (37) gives 5-(*o*-chlorophenyl)hydantoin, m.p. 175.7–176.1° cor. (37).

$\bar{C}$  with hydrazine sulfate gives (91–95% yield (40)) *o*-chlorobenzaldazine, m.p. 143.5° cor., but  $\bar{C}$  with hydrazine hydrate gives (84% yield (40)) *o*-chlorobenzaldehyde hydrazone m.p. 33–34°, b.p. 165–170° at 14 mm.; note that latter on Wolff-Kishner reduction gives (35–82% yield (40)) *o*-chlorotoluene (3:8245).]

① *o*-Chlorobenzaldoxime (*anti* form): pr. from alc., m.p. 75–76° (1) (27). [From  $\bar{C} + NH_2OH.HCl + Na_2CO_3$  (1); the *sym.* isomer has m.p. 98–102° (28), 101–103° (7).]

② *o*-Chlorobenzaldehyde phenylhydrazone: m.p. 86° (29), 84° (39).

③ *o*-Chlorobenzaldehyde *p*-nitrophenylhydrazone: or. pl., m.p. 249° (30) (31); br.-red. ndls., 241° (32); red ndls. from alc., 237–238° (13).

④ *o*-Chlorobenzaldehyde 2,4-dinitrophenylhydrazone; or.-red. ndls. from xylene, m.p. 209° (33), 213.6° (34) 207° (41). [Use in detn. of  $\bar{C}$  (11).]

⑤ *o*-Chlorobenzaldehyde dimethone: ndls. from alc., m.p. 199° u.c., 205° cor. (35). [Corresp. anhydride, cryst. from alc., m.p. 224–226° cor. (35).]

⑥ *o*-Chlorobenzaldehyde semicarbazone: lfts. from MeOH, m.p. 229–230° (36), tpls. from pyridine, m.p. 225–226° (9), 226° (42).

3:6410 (1) Erdmann, Schwechten, *Ann.* 260, 55–58 (1890). (2) Mayer, English, *Ann.* 417, 78 (1918). (3) Kabovec, Kohlrausch, *Z. anorg. Chem.* 7, 211–212 (1897). (4) Zetsche, *Monatsh.* 72, 3, 300 (1901). (5) Zetsche, *Monatsh.* 72, 3, 300 (1901). (6) Zetsche, *Monatsh.* 72, 3, 300 (1901). (7) Zetsche, *Monatsh.* 72, 3, 300 (1901). (8) Gulliard, Monet, *Chem. Soc.* 93, 1636 (1903). (9) Eitel, *Lock, Monatsh.* 72, 3, 300 (1901). (10) Zetsche, *Monatsh.* 72, 3, 300 (1901).

(11) Eitel, *Lock, Monatsh.* 72, 3, 300 (1901). (12) Zetsche, *Monatsh.* 72, 3, 300 (1901). (13) Zetsche, *Monatsh.* 72, 3, 300 (1901). (14) Erdmann, Kirchhoff, *Ann.* 247, 308 (1889). (15) Rosenmund, Zetsche, *Ber.* 54, 436–437 (1921). (16) Henry, *Ber.* 2, 186 (1869). (17) van der Beek, *Rec. trav. chim.* 51, 411–413 (1932). (18) Carruthers, Adams, *J. Chem. Soc.* 1933, 1000 (1933). (19) Zetsche, *Monatsh.* 72, 3, 300 (1901). (20) Eitel,

*Ann.* 478, 128

(24) Will-

(5) Erdmann,

*J. Chem. Soc.* 125, 551 (1924). (25) Behrend,

Frohlich, *Cent.* 1903, II 427. (30) Chatterway,

*Chem.* (2) 144, 312 (1936). (33) Blankens, Wacker, *Rec. trav. chim.* 55, 653 (1936). (34) Ferrante, Bloom, *Am. J. Pharm.* 105, 381–384 (1933). (35) Vorländer, *Z. anal. Chem.* 77, 203 (1929). (36) Henderson, Heilbron, *J. Chem. Soc.* 64, 522–523 (1942). (38) K

14-A, 112–113 (1942).

(40) Lock,

(41) Gra

5–11 (1943).

(42) Vogelsang, *Rec. trav. chim.* 62,

3:6420 1,2,4-TRICHLOROBENZENE  
(*unsym.*-trichlorobenzene)

 $C_6H_3Cl_3$ 

Beil. V - 204

V<sub>1</sub>-(112)V<sub>2</sub>-(156)

B.P.		M.P.		
213° cor.	(1) (17)	17-18°	(8)	$D_{25}^{25} = 1.4634$ (15)
212.9-213°	(2)	17°	(7) (9)	cf. (7)
212-213°	(3)	16-17°	(4)	$n_D^{25} = 1.5524$ (15)
211° cor. at 742 mm.	(4)	16.6°	(10)	
210°	(5) (6)	16.5°	(11) (12)	
206°	(7)	16°	(1) (3) (13)	
		14.5°	(14)	

For thermal annl. of mixts. of  $\bar{C}$  with 1,2,3-trichlorobenzene (3:0990) or with 1,3,5-trichlorobenzene (3:1400) see (10) (the eutectic of  $\bar{C}$  with the former conts. 71%  $\bar{C}$  and melts 2.7° (10)); for m.p./compu. data on ternary mixt. of  $\bar{C}$  with the other two isomers see (10).

[For use of  $\bar{C}$  in mfg. of elec. insulating material see (16).]

[For prepn. of  $\bar{C}$  from 2,4-dichloroaniline [Beil. XII-621; XII<sub>1</sub>-(309)] (1) (11), from 2,5-dichloroaniline [Beil. XII-625, XII<sub>1</sub>-(311)] (6), or 3,4-dichloroaniline [Beil. XII-626 XII<sub>1</sub>-(311)] (1) via diazotization and use of  $Cu_2Cl_2$  reaction see indic. refs.; from 4-chloro-1,3-diaminobenzene [Beil. XIII-53, XIII<sub>1</sub>-(15)] via tetrazotization and use of  $Cu_2Cl_2$  reaction (62% yield) see (17); from *p*-dichlorobenzene (3:0980) with  $S_2Cl_2$  in  $SO_2Cl_2$  +  $AlCl_3$  (58% yield  $\bar{C}$ ) see (3) (18).]

[For formn. of  $\bar{C}$  from 2,3,6-trichlorobenzaldehyde (3:2287) by KOH fusion (88% yield (4)) or from 2,3,6-trichloroacetophenone by KOH fusion (82% yield (14)) see indic. refs.; from 2,4-dichlorophenol (3:0560) by htg. 7 hrs. with  $PCl_5$  (25.5% yield) see (1); from 2-nitro-1,4-dichlorobenzene or from 4-chloro-3-nitrobenzenesulfonic acid by btg. with  $SOCl_2$  in s.t. 10 hrs. at 160-180° see (19) (20); from 2-chlorobenzene-1,4-disulfonyl chloride with  $PCl_5$  in s.t. 4 hrs. at 210° see (8); from 2,4-dichlorobenzene-sulfonyl chloride by htg. with  $SOCl_2$  in s.t. at 180° see (21).]

[For formn. of  $\bar{C}$  (together with other products) from  $C_6H_6$  with  $Cl_2$  in pres. of  $I_2$  (7) or of Fe (22) see indic. refs.; from *o*-dichlorobenzene (3:6055) and/or *p*-dichlorobenzene (3:0980) with  $Cl_2$  under various conditions see (22) (23) (24) (25) (9); from *m*-dichlorobenzene (3:5960) with  $Cl_2$  under various conditions see (9) (13) (23); from chlorobenzene (3:7903) or *p*-dichlorobenzene (3:0980) by boilg. with  $FeCl_3$  see (26); from  $\alpha$ -benzene-hexachloride (3:4410) on htg. above its m.p. (158°) (28) (21) or htd. with aq. in s.t. at 200° (27), or on boilg. with  $MeOH/KOH$  (10),  $EtOH/KOH$  (10) (28) (5) (22), alc. KCN (27), or pyridine (10), or on htg. with quinoline at 105-110° (10), see indic. refs.; from  $\beta$ -benzene-hexachloride (3:4990) q.v. on boilg. with alc. KOH see (10).]

[ $\bar{C}$  with  $Cl_2$  in pres. of Al/Hg yields exclusively (23) 1,2,4,5-tetrachlorobenzene (3:4115), m.p. 135-136° (23);  $\bar{C}$  with liq.  $Cl_2$  in s.t. at room temp. for 10 days gives (29) (30) a mixt. of addn. products.]

[ $\bar{C}$  with  $NuOMe$  in  $MeOH$  under various conditions (31) (32) (33) (11) (34) yields 2,5-dichlorophenol (3:1190), m.p. 57°; for behavior with  $EtOH/KOH$  see (38).]

$\bar{C}$  on mononitration, e.g., by soln. of  $\bar{C}$  (1 g.) in 5 ml. fuming  $HNO_3$  ( $D = 1.49$ ) (35), then pouring onto ice (35), gives 100% yield (35) (1) (5) (15) (39) 1,2,4-trichloro-5-nitrobenzene [Beil. V-246], pr. from alc., m.p. 53° (1), 57° (7) (15), 56° (35); this prod. with piperidine as directed (36) yields 1,2-dichloro-4-piperidino-5-nitrobenzene, red pr. from alc., m.p. 64-65° (36).

$\bar{C}$  on dinitration, e.g., by soln. of  $\bar{C}$  (1 g.) in 5 ml. fuming  $\text{HNO}_3$  ( $D = 1.49$ ) + 5 ml. conc.  $\text{H}_2\text{SO}_4$  and subsequent refluxing for 1 hr., then pouring into aq. (35), gives (100% yield (35)) (7) (37) 1,2,4-trichloro-3,5-dinitrobenzene [Beil. V-266], pr. from alc., m.p. 103.5° (7), 102.5–103.5° (35) (37); this prod. (1 g.) htd. 1 hr. at 100° with 5 g. aniline as directed (35) yields 1-chloro-2,4-dianilino-3,5-dinitrobenzene, m.p. 182° (35).

Note that the trinitration prod. to be expected from complete nitration of  $\bar{C}$  has not been reported.

$\bar{C}$  with chlorosulfonic acid as directed (35) yields 1,2,4-trichlorobenzenesulfonyl chloride, m.p. 31–34° (35) which with  $(\text{NH}_4)_2\text{CO}_3$  yields 1,2,4-trichlorobenzenesulfonamide, m.p. above 200° (35).]

3:6420 (1) Beilstein, Kurbatow, *Ann.* 192, 230–232 (1878). (2) Dadiou, Pongratz, Kohrausch, *Monatsh.* 61, 433 (1932). (3) Süberrad, *J. Chem. Soc.* 121, 1015–1020 (1922). (4) Lock, *Ber.* 66, 1531 (1933). (5) Lesimple, *Ann.* 137, 122–124 (1866). (6) Noeltling, Kopp, *Ber.* 38, 3509 (1905). (7) Jungfleisch, *Ann. chim.* (4) 15, 264–277 (1868). (8) Olivier, *Rec. trav. chim.* 39, 502 (1920). (9) Mouneyrat, Pouret, *Compt. rend.* 127, 1028 (1898). (10) van der Linden, *Ber.* 45, 231–247 (1912).

(11) van der Lande, *Rec. trav. chim.* 51, 104, 110 (1932). (12) Hassel, Naeshagen, *Z. physik. Chem.* B-12, 87 (1931). (13) Olivier, *Rec. trav. chim.* 39, 411–413 (1920). (14) Lock, Böck, *Ber.* 70, 924 (1937). (15) T. Cent. 1923, I 2370, C A 22 U.S. 2,139,945–2,139,948, I Cohn, Fischer, *Monatsh.* 21 1923; Cent. 1923, I 904. Ger. 280,739, Cent. 1913, I 104.

(21) Quilico, *Gazz. chim. ital.* 57, 500 (1927). (22) Zil'berman, Slobodnik, *J. Applied* (1938); C.A. 32, 1664 (1938). (23) Britton (to Dow Chem. Co.), U.S. (1933). (25) Slobodnik, Zil'berma

Thomas, *Compt. rend.* 126, 1212 (1898). (27) Meunier, *Ann. chim.* (6) 10, 223–269 (1887). (28) Matthews, *J. Chem. Soc.* 59, 165–172 (1891). (29) van der Linden, *Rec. trav. chim.* 55, 315–324 (1936). (30) van der Linden, *Rec. trav. chim.* 57, 217–224 (1938). (31) Holleman, *Rec. trav. chim.* 37, 201 (1918). (32) Kraay, *Rec. trav. chim.* 49, 1087 (1930). (33) de Crauw, *Rec. trav. chim.* 50, 787 (1931). (34) Aktien-Gesell. für Anilin Fabrikation, Ger. 349,794, March 9, 1922, Cent. 1922, IV 45. (35) Huntress, Carten, *J. Am. Chem. Soc.* 62, 512–514 (1940). (36) LeFevre, Turner, *J. Chem. Soc.* 1927, 1116–1117. (37) Hüffer, *Rec. trav. chim.* 40, 452 (1920). (38) Clark, Crozier, *Trans. Roy. Soc. Can.* (3) 19, III 153–156 (1925). (39) Holleman, van Haeften, *Rec. trav. chim.* 40, 71 (1921).

—  $p$ -CHLOROBENZYL CHLORIDE



$\text{C}_7\text{H}_5\text{Cl}_2$

Beil. V - 297

V<sub>1</sub>-(152)

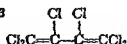
V<sub>2</sub>-(231)

B.P. 214°

M.P. 29–30°

See 3:0220. Division A: Solids.

3:6425 HEXACHLOROBUTADIENE-1,3



$\text{C}_4\text{Cl}_6$

Beil. S.N. 12

B.P.

M.P.

215°

(1)

–21° (1) (2)

$D_4^{20} = 1.6820$  (1)

$n_D^{20} = 1.5542$  (1)

211° at 710 mm. (2)

–19° (5)

[See also octachlorocyclopentene (3:0422).]



Colorless oily liq. with weak turpentine-like odor.

[For prepn. of  $\bar{C}$  from butadiene-1,3 (1) (3) or butane, buteno, or their chloro substitution products (3) (4) with  $Cl_2$ ; or from hexachlorobutene (itself obtd. from dimerization (5) (2) of trichloroethylene (3:5170)) by cat. addn. of  $Cl_2$  followed by cat. removal of 2 HCl or vice versa (1) (2); or from acetylene with  $Cl_2$  (6) (note that tetrachloroethylene (3:5460) is also formed).]

$\bar{C}$  on reduction with Zn + alc. gives (1) butadiene-1,3 (corresp. tetrahydride, m.p. 117°).

$\bar{C}$  behaves as if saturated: e.g.,  $\bar{C}$  does not add  $Cl_2$  (even in sunlight) (1);  $\bar{C}$  does not (1) react with maleic anhydride or benzoquinone-1,4;  $\bar{C}$  does not (1) polymerize (even at 100 atm.).

$\bar{C}$  is stable toward acids and alkalis and (unlike some other highly chlorinated unsaturates) does not give a carboxylic acid on treatment with conc.  $H_2SO_4$  (1).

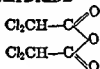
Note that a product of m.p. 38° and b.p. 283° formerly regarded as  $\bar{C}$  is now thought to be octachlorocyclopentene (3:0390).

3:6425 (1) Fruhwirth, *Ber.* 74, 1700-1701 (1941). (2) Consortium für Elektrochem. Ind., French 836,719, Jan. 25, 1939; *Cent.* 1939, I 3256; [*C.A.* 33, 5548 (1939)]; *Ger.* 723,981, July 2, 1942; [*C.A.* 37, 5415 (1934)]. (3) Fruhwirth (to Donau-Chemie, A.G.), *Ger.* 736,884, May 20, 1943; *C.A.* 38, 2974 (1944). (4) Wimmer, Mugdan (to Consortium für Elektrochem. Ind.), *Ger.* 734,682, March 25, 1943; *C.A.* 38, 1245 (1944). (5) Mugdan, Wimmer (to Consortium für Elektrochem. Ind.), *Ger.* 704,179, Feb. 20, 1941; *C.A.* 36, 1116 (1942); U.S. 2,269,600, Jan. 13, 1942; *C.A.* 36, 2670 (1942). (6) Fruhwirth (to Donau-Chemie, A.G.), *Ger.* 734,722, March 25, 1943; *C.A.* 38, 1252 (1944).

### 3:6430 DICHLOROACETIC ACID ANHYDRIDE

 $C_2H_2O_2Cl_4$ 

Beil. II - 204


 $\Pi_1-$   
 $\Pi_2-$ 

B.P.

214-216° dec. (1)

 $D_4^{25} = 1.574$  (1)

140° at 35 mm. (2)

100-102° at 15 mm. (3)

Note that the above name of  $\bar{C}$  is so rendered to emphasize that it is the anhydride of dichloroacetic acid (not a dichlorinated acetic anhydride).

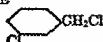
[For prepn. of  $\bar{C}$  from dichloroacetyl chloride (3:5290) with Na $\bar{A}$  in  $POCl_3$  in dry ether (1), or with Na $\bar{A}$  +  $AlCl_3$  (4), or on boilg. with  $Na_2CO_3$  (2) see indic. refs.; for formn. of  $\bar{C}$  as by-product during reactn. of sodium dichloroacetate with acetyl chloride (3:7065) in dry ether see (3) (the other prod. is the mixed anhydride, acetic-dichloroacetic anhydride [Beil. II-204], b.p. 79-80° at 15 mm.,  $D_4^{20} = 1.5170$  (3).]

$\bar{C}$  on hydrolysis with aq. yields dichloroacetic acid (3:6208) q.v.; for the amide, anilide, p-toluidide, and other derivs. corresp. to  $\bar{C}$  see dichloroacetic acid (3:6208).

3:6430 (1) Anthoine, *Jahresber.* 1883, 1032. (2) Patterson, *Ber.* 38, 212-213 (1905). (3) Baroni, *Gazz. chim. ital.* 63, 30 (1933); *Cent.* 1933, I 3183; *C.A.* 27, 3447 (1933). (4) Strosacker, Schwieger (to Dow Chem. Co.), U.S. 1,713,104, May 14, 1929; *Cent.* 1929, II 1215; *C.A.* 23, 3234 (1929).

3:6445 *m*-CHLOROBENZYL CHLORIDE $C_7H_6Cl_2$ 

Beil. V —

 $V_1$ — $V_2$ -(231)

B.P.

215-216° at 753 mm. (1)

 $D_4^{15} = 1.2695$  (1)

213-214° at 740 mm. (2)

111.0-111.2° at 25.4 mm. (3)

111-113° at 25 mm. (4)

110-111° at 25 mm. (5)

104° at 17 mm. (6)

[For prepn. from *m*-chlorobenzyl alc. [Beil. VI-444] with  $PCl_5$  (1) or with  $SOCl_2$  (yield: 87% (5), 78% (4)) see indic. refs.; from *m*-chlorotoluene (3:8275) with  $Cl_2$  see (2) (3) (6) (7) (8) (9) see indic. refs.]

[ $\bar{C}$  with phenol in toluene yields (10) *o*-(*m*-chlorobenzyl)phenol, h.p. 192-194° at 14 mm. (benzoate, m.p. 67-67.4°), and *m*-chlorobenzyl phenyl ether, m.p. 36.0-36.4°;  $\bar{C}$  with 2,4-dichlorophenol (3:0560) in toluene yields (10) 2-(*m*-chlorobenzyl)-4,6-dichlorophenol, m.p. 59.4-60.0° (benzoate, m.p. 63.5-64.0°, benzenesulfonate, m.p. 114.5-115.0°, *p*-toluenesulfonate, m.p. 125.4-126.0°), and *m*-chlorobenzyl 2,4-dichlorophenyl ether, m.p. 42-42.5°.]

[ $\bar{C}$  with phenol +  $AlCl_3$  yields (10) *p*-(*m*-chlorobenzyl)phenol, h.p. 145-148° at 3 mm. (benzoate, m.p. 57.5-58.0°);  $\bar{C}$  with 2,6-dichlorophenol (3:1595) yields (10) 4-(*m*-chlorobenzyl)-2,6-dichlorophenol, m.p. 79-80° (benzoate, m.p. 130-130.4°; *p*-toluenesulfonate, m.p. 104.5-105.0°).]

[ $\bar{C}$  with Mg in dry ether yields (8)  $m-Cl.C_6H_4.CH_2Cl$ ; this on treatment with  $CO_2$  yields  $m-Cl.C_6H_4.CH_2.COOMgCl$  which on subsequent further treatment with various other  $RMgX$  cpds. undergoes abnormal reaction giving *m*-chlorophenylmalonic acid, m.p. 127-128° (8); the  $RMgCl$  cpd. with phenyl isocyanate as directed (13) for the *p*-isomer should yield *m*-chlorophenylacetanilide, m.p. 130° cor. (14), although this reaction has not been specifically reported for  $\bar{C}$ .]

[For studies of rate of reaction of  $\bar{C}$  with  $NaOEt$  see (1) (11) (5); with  $Na_2SO_3$  see (4); with  $AlCl_3 + C_6H_6$  see (12); for acid hydrolysis in acetone see (6); with  $KI$  in various solv. see (6); for reactn. of  $\bar{C}$  with diethyl malonate see (2).]

3:6445 (1) Olivier, *Rec. trav. chim.* 41, 309 (1921). (2) Kenner, Witham, *J. Chem. Soc.* 119, 1460 (1921). (3) de Bruyne, Davis, Gross, *J. Am. Chem. Soc.* 55, 3938 (1933). (4) Sprung, *J. Am. Chem. Soc.* 52, 1643, 1649 (1930). (5) Franzen, Rosenberg, *J. prakt. Chem.* (2) 101, 334 (1921). (6) Bennett, Jones, *J. Chem. Soc.* 1935, 1818. (7) Jones, *J. Chem. Soc.* 1935, 1839. (8) Ivanov, Pehenitchny, *Bull. soc. chim.* (5) 1, 231 (1934). (9) Zelinsky, Schering-Kahlbaum, Ger. 478,084, June 20, 1929; *Cent.* 1929, II 1216. (10) Houston, Guile, Chen, Headley, Warren, Baur, Mate, *J. Am. Chem. Soc.* 55, 4639-4643 (1933).

(11) Olivier, *Rec. trav. chim.* 41, 650 (1921). (12) Olivier, Berger, *Rec. trav. chim.* 45, 717 (1926). (13) Underwood, Gale, *J. Am. Chem. Soc.* 56, 2117-2119 (1934). (14) Jenkins, *J. Am. Chem. Soc.* 55, 2898 (1933).

— *m*-CHLOROPHENOL $C_6H_5OCl$ 

Beil. VI - 185

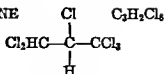
 $V_1$ -( 99) $V_2$ -(172)

B.P. 216°

M.P. 32°

 $D_4^{20} = 1.237$  $n_D^{20} = 1.5565$ 

See 3:0255. Division A: Solids.

**3:6460 1,1,1,2,3,3-HEXACHLOROPROPANE**  
 (unsym.-Hexachloropropane)

 Beil. I —  
 I<sub>1</sub>-(35)  
 I<sub>2</sub>—

 B.P. 216° (1)  
 145° cor. at 90 mm. (1)

 $D_4^{24} = 1.6980$  (1)  $n_D^{17} = 1.5250$  (1)

Colorless liq. [For use as solvent for cellulose esters see (3) (4).]

 [For prepn. of  $\bar{\text{C}}$  from chloroform (3:5050) + trichloroethylene (3:5170) +  $\text{AlCl}_3$  (1) (2) or from  $\text{CCl}_4$  (3:5100) + 1,2-dichloroethylene (3:5030) +  $\text{AlCl}_3$  see (1) (2).]

 $\bar{\text{C}}$  with 1 ml. alc. KOH loses HCl yielding (1) (2) 1,1,2,3,3-pentachloropropene-1 (3:6075), b.p. 183° (1).

 3:6460 (1) Prins, *J. prakt. Chem.* (2) 89, 417-419 (1914). (2) Prins, Ger. 261,689, March 2, 1912; Cent. 1913, II 394; *C.A.* 7, 3641 (1913). (3) Spicers, Ltd. & Hands, Brit. 279,139, April 21, 1926; Cent. 1923, I 770; *C.A.* 22, 2340 (1928). (4) Spicers, Ltd. & Hands, French 625,165, Aug. 4, 1927; Cent. 1923, I 770.

**3:6475 *m*-CHLOROBENZALDEHYDE**
 $\text{C}_7\text{H}_5\text{OCl}$ 

 Beil. VII - 234  
 VII<sub>1</sub>-(133)

 B.P.  
 216.3-216.8° (1)  
 213-214° (2)  
 210.5-211.5° at 740 mm. (3)  
 107-109° at 26 mm. (4)  
 98.6-100.2° at 16 mm. (5)  
 84-86° at 8 mm. (4)

 M.P.  
 17-18° (2)  
 13° (1) (2)

 $D_4^{20.2} = 1.2410$  (6)  
 $n_D^{20.2} = 1.55908$  (6)

 Oil. — Volatile with steam. —  $\bar{\text{C}}$  yields  $\text{NaHSO}_3$  cpd.

 [For prepn. of  $\bar{\text{C}}$  from *m*-nitrobenzaldehyde via reductn. with  $\text{SnCl}_2$  to *m*-aminobenzaldehyde followed by diazotization and reactn. with  $\text{CuCl}$  (yield: 75-79% (4), 70-80% (3), 58-65% (7) (24) see indic. refs.; from *m*-chlorotoluene (3:8275) with  $\text{CrO}_2\text{Cl}_2$  (44.5% yield) see (8); from *m*-chlorobenzyl alc. by oxidn. with  $\text{HNO}_3/\text{H}_2\text{SO}_4$  see (9); for formn. (together with other products) during chlorination of benzaldehyde see (10); from *m*-chlorobenzylamine with formalin + hexamethyleotetramine see (25).]

 $\bar{\text{C}}$  is readily oxidized even by air (4);  $\bar{\text{C}}$  with  $\text{KMnO}_4$  yields *m*-chlorobenzoic acid (3:4392), m.p. 154°. [For study of auto-oxidn. see (11).] —  $\bar{\text{C}}$  with conc. NaOH undergoes Cannizzaro reactn. (for study in dioxane soln. see (23)) although the presumable products, *m*-chlorobenzyl alc., b.p. 234°, and *m*-chlorobenzoic acid, m.p. 154°, have not (by this reactn.) actually been isolated.

 $\bar{\text{C}}$  with dil. alc. KCN at 60° for 5 hrs. in absence of air gives 22% yield of 3,3'-dichlorobenzoin, cryst. from lgr., m.p. 75-76° (12).

 $\bar{\text{C}}$  on hgt. with  $\text{NaOAc} + \text{Ac}_2\text{O}$  for 8 hrs. at 180-200° undergoes Perkin reactn. giving (61.5% yield (13)) *m*-chlorocinnamic acid, m.p. 165° (13) (14). [This with  $\text{Br}_2$  in  $\text{CHCl}_3$  gives dibromide, m.p. 183° (15).] —  $\bar{\text{C}}$  htd. with malonic acid + pyridine (24) gives alm. quant. yield (24) of *m*-chlorocinnamic acid, m.p. 163° (24). [In absence of pyridine reaction gives 100% yield *m*-chlorobenzalmalonic acid, m.p. 184-186° (24).]

 $\bar{\text{C}}$  on mononitration as specified (3) yields 3-chloro-6-nitrobenzaldehyde [Beil. VII-262], ndls. from dil. alc., m.p. 77.5° (3). [Oxime, thls. from alc., m.p. 112° (3); phenylhydrazone, ndls. from alc., m.p. 180-181° (3).]

- ① *m*-Chlorobenzaldoxime (*anti* form): pr. from alc., m.p. 70-71° (2), 70° (16) (17). [From  $\bar{C}$  +  $NH_2OH \cdot HCl$  +  $Na_2CO_3$  (2); the *syn* isomer (from the *anti* via ethereal  $HCl$ , then  $Na_2CO_3$ ) has m.p. 115-116° rap. htg. (2), 118° (17).]
- ② *m*-Chlorobenzaldehyde phenylhydrazone: ndls. from abs. alc., m.p. 134-135° (3), 133-134° (18).
- ③ *m*-Chlorobenzaldehyde *p*-nitrophenylhydrazone: cryst. from dil.  $AcOH$ , m.p. 216° (19), 214° (16). [For m.p./compn. data on mixt. of this deriv. with benzaldehyde *p*-nitrophenylhydrazone, m.p. 190°, see (16).]
- ④ *m*-Chlorobenzaldehyde 2,4-dinitrophenylhydrazone: or.-yel. cryst., m.p. 256° (20), Bordeaux-red cryst. from xylene, m.p. 248° cor. (22), 245° (25). [Use in detn. of  $\bar{C}$  (22).]
- ⑤ *m*-Chlorobenzaldehyde semicarbazone: mts. from  $MeOH$  (21) or pyridine (8), m.p. 230° (21), 228° (8). [This deriv. does not distinguish  $\bar{C}$  from *o*- (3:6410) or *p*- (3:0765) isomers.]

3:6475 (1)  $C_{10}H_7ClO$  (1890). (2)  $C_{10}H_7ClO$  (1890). (3)  $C_{10}H_7ClO$  (1890). (4)  $C_{10}H_7ClO$  (1890). (5)  $C_{10}H_7ClO$  (1890). (6)  $C_{10}H_7ClO$  (1890). (7)  $C_{10}H_7ClO$  (1890). (8) Law, Perkin, *J. Chem. Soc.* 93, 1636-1637 (1908). (9) Mettler, *Ber.* 38, 2812 (1905). (10) Gnehm, Bänziger, *Ann.* 296, 65 (1897). *Ber.* 29, 875 (1896). (11) van der Beek, *Rec. trav. chim.* 61, 412-413 (1932). (12) Weissberger, *J. Chem. Soc.* 1935, 225. (13) Böck, Lock, Schmidt, *Monatsh.* 64, 406 (1934). (14) Reich, Araus, Potok, Tempel, *Helv. Chim. Acta* 3, 794 (1920). (15) Willstaedt, *Ber.* 64, 2693 (1931). (16) Shoppee, *J. Chem. Soc.* 1935, 111. (17) Shoppee, *J. Chem. Soc.* 1935, 111. (18) Shoppee, *J. Chem. Soc.* 1935, 111. (19) Shoppee, *J. Chem. Soc.* 1935, 111. (20) Shoppee, *J. Chem. Soc.* 1935, 111. (21) Shoppee, *J. Chem. Soc.* 1935, 111. (22) Shoppee, *J. Chem. Soc.* 1935, 111. (23) Shoppee, *J. Chem. Soc.* 1935, 111. (24) Shoppee, *J. Chem. Soc.* 1935, 111. (25) Shoppee, *J. Chem. Soc.* 1935, 111.

*J. Gen. Chem. (U.S.S.R.)* 14, 120-127 (1944); *C.A.* 39, 916 (1945). (25) Graymore, Davies, *J. Chem. Soc.* 1945, 293-294. (26) Vogelsang, *Rec. trav. chim.* 62, 5-11 (1943); *C.A.* 39, 1394 (1945).

3:6490 ISOAMYL TRICHLOROACETATE  $C_7H_{11}O_2Cl_3$  Beil. II - 200  
 $iso-C_5H_{11}O.CO.CCl_3$  II<sub>1</sub>-(94)  
 II<sub>2</sub>-(200)

B.P. 217° (1)  $D_4^{20} = 1.2314$  (2) cf. (3)  $n_D^{20} = 1.4521$  (2)

3:6490 (1) Clermont, *Bull. soc. chim.* (2) 40, 302 (1883). (2) Schjanberg, *Z. physik. Chem.* A-172, 229 (1935). (3) Livingston, Morgan, Kramer, *J. Am. Chem. Soc.* 35, 1836 (1913).

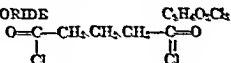
# CHAPTER XV

## DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

### Section 1. $D_4^{20}$ greater than 1.1500

(3:6500-3:6999)

3:6500 GLUTARYL (DI)CHLORIDE



Beil II - 634  
II- (773)  
II- (566)

B.P.

216-218° cor. (1)

107-108° at 16 mm. (2)

100° at 15 mm. (3)

$D_4^{15} = 1.3721$  (2)

$D_4^{20} = 1.324$  (2)  $n_D^{20} = 1.47351$  (2)

[For prepn. of  $\bar{C}$  from glutaric acid (1:0440) with  $\text{PCl}_5$  (1) (2) (3) or with  $\text{SOCl}_2$  (80-88% yield (4)) (5) see indic. refs.]

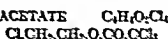
Note that  $\bar{C}$  may react in either *syn.* or *anti.* form (6).

[ $\bar{C}$  with  $\text{AlCl}_3 + \text{C}_6\text{H}_6$  yields (7) (4) 1,5-diphenylpentanedione-1,5 (1,3-diphenylpropane) (Beil. VII-773, VII- (403)), m.p. 62-63° (7) (4);  $\bar{C}$  with  $\text{AlCl}_3 + m$ -xylene gives (8) 1,5-di-*m*-xylylpentanedione-1,5, m.p. 60° (8), +  $\gamma$ -(*m*-xylyl)-*n*-butyric acid, m.p. 115° (8);  $\bar{C}$  with  $\text{AlCl}_3 +$  mesitylene gives (72% yield (5)) 1,5-dimesitylpentanedione-1,5, m.p. 133-134° (5).]

$\bar{C}$  on hydrolysis yields glutaric acid (1:0440), m.p. 96° (for the diamide, diamide, di-*p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see 1:0440).

3:6500 (1) Reboul, *Ann. chim.* (5) 14, 504 (1878). (2) von Auwers, Schmidt, *Ber.* 46, 479 (1915). (3) Meerburg, *Rec. trav. chim.* 18, 373 (1899). (4) Straup, Guggenheimer, *Ber.* 58, 2493 (1925). (5) Kao, *J. Chinese Chem. Soc.* 3, 56-59 (1955). (6) Plant, Tomlinson, *J. Chem. Soc.* 1933, 856. (7) Auger, *Ann. chim.* (6) 27, 338 (1891). (8) Borache, *Ber.* 52, 2060 (1919).

3:6510  $\beta$ -CHLOROETHYL TRICHLOROACETATE



Beil II - 209  
II-  
II-

B.P.

217° at 766 mm. (1)

99.5-100.0° at 14 mm. (2)

95-96° at 11 mm. (3)

68-69° at 1.6 mm. (4)

$D_4^{20} = 1.5357$  (1), cf. (4)

$n_D^{20} = 1.48133$  (1) cf. (4)

[For prepn. (45% yield (3)) from ethylene chlorohydrin (3:5552) + trichloroacetyl chloride (3:5420) + pyridine in ether see (3) (1); for prepn. (70% yield (3)) from  $\beta$ -hydroxyethyl trichloroacetate (3:9099) +  $\text{SOCl}_2$  see (3).]

$\bar{C}$  on shaking with aq. is smoothly saponified to  $\beta$ -chloroethanol (3:5552) + trichloroacetic ac. (3:1150), no chloride ion being formed (3).

3:6510 (1) Delacere, *Bull. soc. chim.* (2) 48, 708 (1887). (2) Palomas, Salmi, Korte, *Ber.* 72, 797 (1939). (3) Meerwein, Sönke, *Ber.* 64, 2380 (1931). (4) Meerwein, Sönke, *J. prakt. Chem.* (2) 137, 309 (1933).

3:6517  $\beta$ -CHLORO- $\beta'$ -HYDROXY-ISOPROPYL ACETATE  $C_6H_9O_3Cl$  Beil. II - 142  
 (Glycerol  $\alpha$ -chlorohydrin  $\beta$ -acetate;  
 $\beta$ -aceto- $\alpha$ -chlorohydrin;  
 $\gamma$ -chloropropylene glycol  $\beta$ -acetate)

$$\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{H}-\text{C}-\text{O}\cdot\text{CO}\cdot\text{CH}_3 \\ | \\ \text{CH}_2\text{OH} \end{array} \quad \begin{array}{l} \text{II}_1-(67) \\ \text{II}_2- \end{array}$$

B.P. 218° (1) at 760 mm. (2)

108° at 12 mm. (3)

[See also glycerol  $\alpha$ -chlorohydrin  $\alpha'$ -acetate (3:6775).]

[For formn. of  $\bar{C}$  from 3-hydroxy-1,2-epoxypropane (glycidol) with  $\text{AcCl}$  (3:7065) ( $\gamma$ -hydroxy- $\beta$ -chloro- $n$ -propyl acetate is also formed) see (1); from epichlorohydrin (3:5358) with  $\text{AcOH}$  in s.t. at 180° see (1); from glycerol  $\alpha,\beta$ -diacetate with  $\text{PCl}_5$  see (3).]

Note that the homogeneity of all reported preps. of  $\bar{C}$  is probably open to serious question.

3:6517 (1) Bigot, *Ann. chim.* (6) 22, 489-491 (1891). (2) Gibson, *J. Soc. Chem. Ind.* 50, 950 (1931). (3) Wegscheider, Zmerzlíkar, *Monatsh.* 34, 1079-1080 (1913).

— 1,2,3-TRICHLOROBENZENE



$C_6H_3Cl_3$

Beil. V - 203

$V_1$ -(112)

$V_2$ -(156)

B.P. 218-219°

M.P. 53-54°

See 3:0990. Division A: Solids.

— 2,6-DICHLOROPHENOL



$C_6H_4OCl_2$

Beil. VI - 190

$VI_1$ -(103)

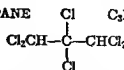
$VI_2$ -(179)

B.P. 219-220° at 740 mm.

M.P. 67°

See 3:1595. Division A: Solids.

3:6525 1,1,2,2,3,3-HEXACHLOROPROPANE  
 (sym.-Hexachloropropane)



$C_3H_2Cl_6$

Beil. I - 107

$I_1$ -(35)

$I_2$ -

B.P. 218.5° (1)

$D_4^{24} = 1.7131$  (1)

$n_D^{18} = 1.5262$  (1)

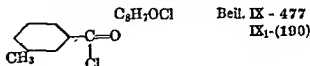
[For prepn. of  $\bar{C}$  from 1,2,3,3-tetrachloropropene-1 (3:5920) +  $\text{Cl}_2$  in sunlight at -30° see (1).] [The product obtd. by (4) from sym.-tetrachloroacetone (3:6050) +  $\text{PCl}_5$  was probably very impure  $\bar{C}$ .]

$\bar{C}$  with alc. KOH loses HCl quant. yielding 1,1,2,3,3-pentachloropropene-1 (3:6075), h.p. 183° (1).

[For use as solvent for cellulose esters see (2) (3).]

(2) Spicers, Ltd. & Hands, Brit. 279,139,  
(3) Spicers, Ltd. & Hands, French 625,165,  
Ann. 252, 335-338 (1889).

3:6535 *m*-TOLUYL CHLORIDE  
(*m*-Methylbenzoyl chloride)



B.P.		M.P.	
219-220°	at 773 mm. (1)	-25° (4)	$D_4^{20} = 1.173$ (3)
218.7-219.7°	at 760 mm. (2)	-23° (1)	
218°	at 724 mm. (1)		
120°	at 38 mm. (3)		
119-120°	at 36 mm. (4)		
[136-138°	at 31 mm. (5)]		
105°	at 20 mm. (6)		
109°	at 15 mm. (7)		
109°	at 8 mm. (8)		
71.2°	at 4 mm. (9)		

[For prepn. of  $\bar{C}$  from *m*-toluic acid (1:0705) with  $PCl_5$  (83% yield (1)) (2) (10), with  $PCl_5$  in  $CHCl_3$  (70% yield (3)) (5), with  $PCl_5$  (8), with  $SOCl_2$  (95% yield (11)) (12) (6) (9), or with  $POCl_3$  + NaCl (or KCl) (13) see indic. refs.; for formn. of  $\bar{C}$  from heptadinyne-1,6-carboxylic acid-4 (*pseudo-m*-toluic acid) with  $PCl_5$  see (14).]

$\bar{C}$  with pyridine and excess  $K_2S_2O_8$  yields (15) *m*-toluic anhydride, m.p. 70-71°.

[For reactn. of  $\bar{C}$  with  $AlCl_3$  and various hydrocarbons to yield corresp. ketones, e.g., with  $C_6H_6$  yielding (10) phenyl *m*-tolyl ketone [Beil. VII-440, VII<sub>1</sub>-(235)], with toluene yielding (16) *m*-tolyl *p*-tolyl ketone [Beil. VII-451], with *m*-xylene yielding (17) *m*-tolyl *m*-tolyl ketone [Beil. VII-815], m.p. 236°.]

43% (19) *m*-methylacetophenone (1:5527), h.p. 220°.]

[ $\bar{C}$  with  $Cl_2$  at 160-180° gives (90% yield (21)) (6) *m*-(chloromethyl)benzoyl chloride ( $\omega$ -chloro-*m*-tolyl chloride), h.p. 149-150° at 20 mm. (21);  $\bar{C}$  with  $Br_2$  at 185-195° gives (50% yield (22))  $\omega$ -bromo-*m*-tolyl bromide, h.p. 167° at 22 mm. (22).]

[ $\bar{C}$  with MeOH yields methyl *m*-toluate (1:3781), h.p. 221°;  $\bar{C}$  with EtOH yields ethyl *m*-toluate (1:3942), h.p. 234°; for study of rate of reactn. see (4).]

$\bar{C}$  on hydrolysis yields *m*-toluic acid (1:0705), m.p. 110-111° (for study of rate see (23)).  
— For the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see *m*-toluic acid (1:0705).

3:6535 (1) van Scherpenzeel, *Rec. trav. chim.* 20, 162 (1901). (2) Kohlrausch, Pongratz, Stock-  
mair, *J. Am. Chem. Soc.* 310. (6)  
Morgar 94 (1899).  
(8) Fra *Im. Chem.*  
Soc. 58.  
(11) .. ) Shopee.

*J. Chem. Soc.* 1932, 700. {13} Kissling (to I.G.), *Ger.* 642,519, March 10, 1937; *Cent.* 1937, I, 3874; *C.A.* 31, 5816 (1937). {14} Perkin, Simonsen, *J. Chem. Soc.* 91, 847 (1907). {15} Gasopoulos, *Praktika Akad. Athina* 6, 347-353 (1931); *Cent.* 1932, I 3171. {16} Seharwin, Schorygin, *Ber* 36, 2027 (1903). {17} Morgan, Coulson, *J. Chem. Soc.* 1929, 2213. {18} Seer, *Monatsh.* 32, 154-157 (1911). {19} Mauthner, *J. prakt. Chem.* (2) 103, 394 (1921/22). {20} Gilman, Nelson, *Rec. trav. chim.* 55, 528-530 (1936).  
 {21} Titley, *J. Chem. Soc.* 1928, 2582. {22} Davies, Perkin, *J. Chem. Soc.* 121, 2210 (1922).  
 {23} Berger, Olivier, *Rec. trav. chim.* 46, 524-527 (1927).

3:6540 BENZOTRICHLORIDE  
 (Phenylchloroform,  
 $\omega, \omega, \omega$ -trichlorotoluene)



$C_7H_5Cl_3$  Beil. V - 300  
 $V_1$ -(152)  
 $V_2$ -(233)

B.P.		F.P.		
220.5-221.5°	(1)	-4.4°	(8)	$D_4^{20} = 1.3741$ (8)
220.9°	(2)	-4.75°	(3)	1.37563 (4)
220.7° at 761 mm.	(3)	-5.0°	(9) (10)	$n_D^{20} = 1.55789$ (8)
214-216°	(4)	-8.1°	(7)	1.5579 (4)
213.0-213.5°	(5)			1.55726 (11)
129° at 60 mm.	(6)			$D_{-15}^{15} = 1.3775$ (3)
105° at 25 mm.	(7)			
110.7° at 23 mm.	(3)			
89.0-89.5° at 10 mm.	(8)			

Colorless liquid insol. aq., sol. many org. solvents. — Ord. samples of  $\bar{C}$  may also cont. benzal (di)chloride (3:6327) or even benzyl chloride (3:8535). —  $\bar{C}$  when pure is stable in dry air, but ord. material (contg. dislvd. HCl) hydrolyzes rapidly in moist air (3). — The very high value (93) of molal f.p. lowering of  $\bar{C}$  prob. accounts for difficulty of earlier workers in attaining high f.p. values (3). — For removal of dislvd. HCl from  $\bar{C}$  by treat. with  $PbCO_3$  see (9). — For purification of  $\bar{C}$  via crystallization see (10); for comml. purification see (12).

$\bar{C}$  forms const.-boilg. mixts. with various cpds., e.g.,  $\bar{C}$  with *p*-dibromobenzene (b.p. 220.25°) forms an azeotrope, b.p. 219.6° at 760 mm., contg. 28 wt. %  $\bar{C}$  (2);  $\bar{C}$  with nitrobenzene (b.p. 210.75°) forms an azeotrope, b.p. 210.72° at 760 mm., contg. 1.5 wt. %  $\bar{C}$  (2);  $\bar{C}$  with *o*-nitrotoluene (b.p. 221.85°) forms an azeotrope, b.p. 219.55° at 760 mm., contg. 75.5 wt. %  $\bar{C}$  (13);  $\bar{C}$  with methyl salicylate (1:1750) (b.p. 222.35°) forms an azeotrope, b.p. 220.75° at 760 mm., contg. 97 wt. %  $\bar{C}$  (13).

$\bar{C}$  is impt. intermediate in prepn. of benzoic acid (see below under hydrolysis), in prepn. of certain dyestuffs (see below), and in prepn. of acyl halides and anhydrides (see below); for use in prepn. of films of cellulose ethers see (14).

[For prepn. of  $\bar{C}$  from toluene with  $Cl_2$  especially in pres. of light and/or other catalysts see (15) (16) (17) (18); with  $Cl_2$  in pres. of  $PCl_3$  (3) cf. (19); with  $SOCl_2$  in s.t. at 220° for 18 hrs. (20) or at 230-250° (21) see indic. refs.; with  $NOCl$  at 350° see (22); for formn. of  $\bar{C}$  from benzal (di)chloride (3:6327) with  $Cl_2$  (23) or with  $NOCl$  at 150° (24) see indic. refs.; from benzyl chloride (3:8535) by htg. with  $PhCl_4 \cdot 2NH_4Cl$  see (25); from benzoyl chloride (3:6240) with  $PCl_5$  see (26); from benzotrifluoride + acetyl chloride +  $AlCl_3$  as directed see (8); from benzyl ethers with  $PCl_5$  see (27).]

[ $\bar{C}$  on reductn. in alc. soln. with  $H_2$  in pres. of colloidal Pd (28) or  $Pd/CaCO_3$  (29) reacts bimolecularly giving (75% yield (28)) toluene tetrachloride (diphenylacetylene tetrachloride) (3:4496), colorless cryst. from  $AcOH$ , m.p. 162-163° (28), also obt'd. from  $\bar{C}$  by other treatments (see below); this prod. with  $H_2$  +  $Pd/CaCO_3$  in alc. KOH is further reduced yielding (29) dibenzyl (1:7149) (use in quant. detn. of its halogen (29)). —  $\bar{C}$  with hydra-



zine hydrate in MeOH/KOH in pres. of Pd/CaCO<sub>3</sub> refluxed for 1½ hrs. gives (42% yield (30)) a mixt. of the two geom. isomeric tolane dichlorides consisting mainly of the  $\alpha$ -isomer (3:4210), colorless tbls. from alc., m.p. 148° (30), with a little of the  $\beta$ -isomer (3:1380), m.p. 61° (30); despite their unsaturation these prods. reduce further only with difficulty.

[ $\bar{C}$  satd. with Cl<sub>2</sub> and stood in sunlight for 8 months or  $\bar{C}$  with liq. Cl<sub>2</sub> in sunlight for a few days adds 3 Cl<sub>2</sub> yielding (31) 1,2,3,4,5,6-hexachloro-1 (trichloromethyl)cyclohexane, cryst. from CHCl<sub>3</sub> or by sublimation, m.p. 103° (31); this may be accompanied by a little pentachlorotrichloromethylcyclohexene, m.p. 132–134° (31). —  $\bar{C}$  with Cl<sub>2</sub> in pres. of I<sub>2</sub> yields (32) a mixt. of mono- and di-chlorobenzotrichlorides.]

[ $\bar{C}$  on pyrogenic decompn. over Pt at red heat yields (32a) cf. (34) tolane tetrachloride (3:4496) together with its isomorphous mixt. with  $\alpha$ -tolano dichloride (see above). —  $\bar{C}$  with Na in liq. NH<sub>3</sub> yields (33) 5% dibenzyl (1:7149) accompanied by much nitrogenous tar. —  $\bar{C}$  with Zn in ether soln. reacts vigorously yielding (35) a deep green sola. contg. tolane dichloride (see above). —  $\bar{C}$  with equal wt. reduced Cu at 100° for 10 hrs. yields (36) tolane tetrachloride, m.p. 162° (3:4496); note that distn. of crude reactn. prod. leads to further reactn. and formation (36) (37) of  $\alpha$ - and  $\beta$ -tolane dichlorides (see above). —  $\bar{C}$  with C<sub>6</sub>H<sub>6</sub> in pres. of powdered chromium metal at 100° for 5 hrs. gives (17% yield (38)) triphenylchloromethane (3:3410), m.p. 106° (38). —  $\bar{C}$  with small proportion of AlCl<sub>3</sub> (0.1 mole) at 50–60° evolves HCl and gives a mixt. (39) contg. 40%  $\alpha,\alpha$ -dichloro-*m*-trichloromethyl-diphenylmethane, m.p. 50–61°, + 10% *m*-( $\alpha,\alpha'$ -dichloro-*m'*-trichloromethylbenzyl)- $\alpha,\alpha$ -dichlorodiphenylmethane, oil, + 34% unchanged  $\bar{C}$ . —  $\bar{C}$  with AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> (39) or  $\bar{C}$  with Al + HgCl<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> (40) gives (62% yield (39)) 0,0',10,10'-tetraphenyl-0,10-dihydroanthracene, cryst. from acetone or lgr., m.p. 159° (40), 157–158° (39).]

[ $\bar{C}$  with MeMgCl in ether gives two types of reactn. according to concn. (41); e.g.,  $\bar{C}$  with dilute MeMgCl yields tolane tetrachloride (3:4496) + ethano + MgCl<sub>2</sub>, while  $\bar{C}$  with conc. MeMgCl gives in 22% yield a mixt. of the two geom. isomers of tolane dichloride (see above) consisting of 5 pts. of the *trans* form (3:4210), m.p. 138–139° (41), together with 1 pt. of the *cis* form (3:1380), m.p. 63° (41), separable by fractional crystn. from alc. — For reactn. of  $\bar{C}$  with EtMgBr see (42). —  $\bar{C}$  does not (43) react with excess mercury di-*p*-tolyl.]

[ $\bar{C}$  with HF gas in Cu flask at 0° for 72 hrs. (44), or  $\bar{C}$  with SbF<sub>3</sub> (45) (46), or  $\bar{C}$  with SbF<sub>3</sub>.2NaF at 130–140° (47), gives yields; 75–95% (44), 75% (45), benzotrifluoride, b.p. 102.3°, m.p. –29°. — Note that  $\bar{C}$  with ZnF<sub>2</sub> in Cu flask at 120° for 6 hrs. gives (65% yield (57)) benzoyl fluoride, b.p. 155–156° (57), also that  $\bar{C}$  + KF in HCOOH gives (16% yield (58)) formyl fluoride, b.p. –26° at 750 mm. (58).]

$\bar{C}$  on complete hydrolysis yields benzoic acid (1:0715): e.g.,  $\bar{C}$  on htg. with anhydrous HCOOH yields (48) BzOH + CO + HCl (use in detn. of side-chain halogen (49));  $\bar{C}$  with aq. in s.t. at 150° (15) or with aq. at 90–95° in pres. of Fe salts (50), or with aq. vapor at 550–850° over cat. (51), or with aq. + ZnCl<sub>2</sub> at 110–115° under press. (52), or with aq. CaCO<sub>3</sub> at 90° followed by acidif. with minl. acid (53) yields BzOH; note, however, although  $\bar{C}$  in ether soln. is only slowly hydrolyzed by aq. at room temp. (54) yet  $\bar{C}$  adequately shaken with aq. at room temp. is completely hydrolyzed (use in detn. of  $\bar{C}$  + benzal (di)-chloride + benzyl chloride by titration with std. alk. using thymolsulfonphthalein (55)) and  $\bar{C}$  if subjected to actn. of steam (as in steam distn. of mixt. with volatile cpds.) is partially hydrolyzed (8). — [For study of kinetics of hydrolysis of  $\bar{C}$  in aq. acetone at 30° in pres. of acids, bases, or salts see (1).]

[ $\bar{C}$  on partial hydrolysis yields benzoyl chloride (3:6240): e.g.,  $\bar{C}$  with limited amt. aq. in pres. of H<sub>2</sub>SO<sub>4</sub> or FeCl<sub>3</sub> (56), or  $\bar{C}$  with ord. comml. ZnCl<sub>2</sub> at 120° (57) (58), or  $\bar{C}$  with aq. vapor over tin phosphate at 240° (59), or  $\bar{C}$  with pure ZnO at 100° (57), or  $\bar{C}$  with benzoic

acid in boilg. nitrobenzene (60), yields  $BzCl$ ; note, however, that  $\bar{C}$  with pure  $ZnCl_2$  fails to react but addn. of 1 mole aq. or initial use of tech.  $ZnCl_2$  gives  $BzCl$  (57).]

[ $\bar{C}$  htd. with carboxylic acids or anhydrides especially in pres. of  $ZnCl_2$  is often used to prepare a mixture of benzoyl chloride with the acid chloride of the acid employed, particularly in cases where the two acyl chlorides are readily separable: e.g.,  $\bar{C}$  with phthalic anhydride (1:0725) (61) (62) or phthalic acid (1:0820) (62) +  $ZnCl_2$  at 110–120° or above gives 96% yield  $BzCl$  (3:6240) + 93% *sym.*-phthalyl (di)chloride (3:6900); for other examples see under chloroacetyl chloride (3:5235), dichloroacetyl chloride (3:5290), trichloroacetyl chloride (3:5420), fumaryl (di)chloride (3:5875), and terephthalyl (di)chloride (3:2205). — Similarly  $\bar{C}$  with salts of sulfonic acids yields  $BzCl$  + the corresp. sulfonyl chloride: e.g.,  $\bar{C}$  + sodium  $\beta$ -naphthalenesulfonate gives (63) 90% yield  $BzCl$  + 80% yield  $\beta$ -naphthalenesulfonyl chloride.]

[ $\bar{C}$  under certain conditions may be converted to benzoic anhydride (1:0595): e.g.,  $\bar{C}$  with  $BzOH$  + trace Fe salts htd. 6 hrs. at 110–115° under reflux (64), or  $\bar{C}$  with  $NaOBz$  (65), or  $\bar{C}$  with ord. conc.  $H_2SO_4$  (66), or  $\bar{C}$  in  $AcOH$  in pres. of phosgene (67), yields  $Bz_2O$ .]

$\bar{C}$  very readily undergoes alcoholysis: e.g.,  $\bar{C}$  with  $EtOH$  in pres. of  $ZnCl_2$  yields (69) ethyl benzoate (1:3721); note, however, that  $\bar{C}$  + abs.  $EtOH$  in s.t. at 130–140° (70) or  $\bar{C}$  + trace sublimed  $FeCl_3$  treated at 80–110° with 95% alc. (71) yields benzoyl chloride (3:6240) + ethyl chloride (3:7015); furthermore that  $\bar{C}$  + ethyl acetate (2 moles) in pres. of  $ZnCl_2$  yields (69) ethyl benzoate (1:3721) + acetyl chloride (3:7065) + ethyl chloride (3:7015).

$\bar{C}$  reacts with phenols to give various products according to circumstances:  $\bar{C}$  with aq. (72) (74) or better alc. (73) sodium phenolate (3 mmoles) gives at 100° small yields of phenyl benzoate (1:2257), m.p. 71°, and of *o*-hydroxybenzophenone (1:1414), m.p. 41°, together with other prods. notably benzaurin (see below). —  $\bar{C}$  with phenol in pres. of  $ZnO$  gives (75) phenyl benzoate (see above) + *p*-hydroxybenzophenone (1:1500), m.p. 134°. —  $\bar{C}$  with phenol (2 moles) htd. at 100° and reactn. prod. treated with steam yields (76) (77) 4,4'-dihydroxytriphenylcarbinol (=phenolbenzein=4'-hydroxyfuchson=benzaurin) [Beil. VI-1145, VIII<sub>1</sub>-(589)], as red crystn. powder (diacetate, m.p. 119° (76) (77); dibenzoate, m.p. 153–154° (76)), accompanied by *p*-hydroxybenzophenone (see above). — [For corresp. reactns. of  $\bar{C}$  with *o*-cresol (1:1400) yielding *o*-cresolbenzein (78) (79), with thymol (1:1430) yielding thymolbenzein (80), with resorcinol (1:1530) yielding resorcinolbenzein (76), or with pyrogallol (1:1555) yielding pyrogallolbenzein (81) see indic. refs. — For reactn. of  $\bar{C}$  with  $\alpha$ -naphthol (1:1500) (73) (94) (95) (or with 1-hydroxynaphthoic acid-2 (82) (83) (95)) yielding 4-(1-hydroxynaphthyl) phenyl ketone (or the corresp. 4-(1-hydroxy-2-carboxynaphthyl) phenyl ketones) respectively see indic. refs.; for reactn. of  $\bar{C}$  with  $\beta$ -naphthol (1:1540) see (84).]

$\bar{C}$  with ammonia or amines gives varied reactns. —  $\bar{C}$  with liq.  $NH_3$  (85) or with  $NH_4Cl$  in s.t. at 200° (86) gives (75% yield (85)) benzonitrile;  $\bar{C}$  with conc. aq.  $NH_4OH$  in s.t. at 130° yields (85) benzoic acid + benzamide + benzonitrile. —  $\bar{C}$  (1 mole) with aniline (2 moles) warmed together without solvent or with  $ZnCl_2$  in  $AcOH$  soln. gives (87) *N,N'*-diphenylbenzamidine hydrochloride [Beil. XII-273, XII<sub>1</sub>-(202)], the free base of which has m.p. 147°; note, however, that  $\bar{C}$  with aniline hydrochloride + nitrobenzene + Fe filings htd. at 180° for 3–4 hrs. yields (87) the dyestuff Doebner's Violet (the  $HCl$  reactn. prod. of 4,4'-diaminotriphenylcarbinol) [Beil. XIII-742, XIII<sub>1</sub>-(293)]. —  $\bar{C}$  (1 mole) with dimethylaniline (2 moles) htd. at 100° preferably in pres. of  $ZnCl_2$  yields (86) the dyestuff Malachite Green (the  $HCl$  reactn. prod. of 4,4'-dimethylaminotriphenylcarbinol) [Beil. XIII-743, XIII<sub>1</sub>-(293)] (see  $\textcircled{P}$  below); analogous dyestuffs from other tertiary amines cannot be discussed here.

[ $\bar{C}$  with excess phenylhydrazine in alc. does not react until Cu powder is added; the

solution then (89) rapidly turns or.-red. and on cooling soon ppts. a mixture of benzaldehyde-phenylhydrazon, m.p. 157° (see 1:0195) (doubtless accounted for by reductn. of  $\bar{C}$  to benzal (di)chloride (3:6327) at the expense of phenylhydrazine), together with phenylhydrazine hydrochloride. —  $\bar{C}$  + excess phenylhydrazine heated in alc. without Cu (89) turns dark red and ppts. a mixt. of "formazylbenzene" [Beil. XVI-17], red lfts. from alc., m.p. 173° (doubtless accounted for as above), and phenylhydrazine hydrochloride.]

[ $\bar{C}$  with amides or ammonium salts gives on htg. mixtures of corresp. nitriles and acid halides: e.g.,  $\bar{C}$  with benzamide at 140° yields (90) benzonitrile + benzoyl chloride;  $\bar{C}$  with *p*-toluamide at 140° yields (90) benzonitrile, *p*-tolunitrile, benzoyl chloride, and *p*-toluyl eldride (3:6000). — For patents exemplifying this type of reactn. see (91) (92).]

$\bar{C}$  on mononitration, e.g., with 0.44 pt. fuming  $\text{HNO}_3$  + 0.44 pt. conc.  $\text{H}_2\text{SO}_4$  at 25-30° for  $\frac{1}{2}$  hr. (4), gives 85% yield *m*-nitrobenzoic acid, m.p. 140° (4); very possibly hydrolysis here precedes nitration since  $\bar{C}$  on nitration with  $\text{N}_2\text{O}_5$  in cold  $\text{CCl}_4$  gives (32) (93) an oily mixt. of nitrobenzotrichlorides more stable to hydrolysis than original  $\bar{C}$ , but which on cleavage with alk. or conc.  $\text{H}_2\text{SO}_4$  yields a mixt. of nitrobenzoic acids containing 70% *m*-nitrobenzoic acid (for other studies of nitration of  $\bar{C}$  see (5) (10)). —  $\bar{C}$  on dinitration by sola. in 5.4 pts. conc.  $\text{H}_2\text{SO}_4$  and treatment with 6.8 pts. fuming  $\text{HNO}_3$  at 185° for 1 hr. gives (4) 33% yield of 3,5-dinitrobenzoic acid, m.p. 203-204° (4).

[ $\bar{C}$  cannot be sulfonated without hydrolysis of the  $-\text{CCl}_3$  group;  $\bar{C}$  with conc.  $\text{H}_2\text{SO}_4$  even at 30° yields (66) benzoic acid (or its anhydride). — However,  $\bar{C}$  with gaseous  $\text{SO}_2$  at room temp. (6) gives on subsequent vac. distn. an oil (perhaps *m*-sulfobenzotrichloride) which with aq. yields *m*-sulfobenzoic acid [Beil. XI-384, XI-(98)], dihydrate, m.p. 67-68°, losing aq. at 100° yielding anhydrous acid, m.p. 140-141° (6).]

⑤ Malachite Green formation.  $\bar{C}$  (1 drop) + dimethylaniline (1 drop) warmed with 0.1 g. fused  $\text{ZnCl}_2$  gives intense green color.

⑥ Benzoic acid:  $\bar{C}$  on refluxing with aq.  $\text{NaOH}$  soln., subsequently acidified, ppts. benzoic acid (1:0715), m.p. 121°.

3:6540 (1) Olivier, Weber, *Rec. trav. chim.* 53, 881, 884 (1934). (2) Locat, *Rec. trav. chim.* 47, 14, 17 (1928). (3) Swarts, *Bull. soc. chim. Belg.* 31, 376-377 (1922). (4) Sah, Lei, Wang, *Sci. Repts. Natl. Tsinghua Univ.* A-2, 137-Flüschheim, Holmes, *J. Chem. Soc.* 11, 258 (1935); (2) 143, 127-138 (1935). *Cent.* 1914, I 618. (8) Hénne, *Newman Roy. Soc. London A-133*, 673 (1931). (1914).

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(3) (191-2825  
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Clar,  
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Vohl,

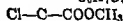
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*Ann.* **217**, 239-249 (1883). {62} Fireman, *J. Am. Chem. Soc.* **52**, 2951-2954 (1930). {63} Doebner,  
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## 3:6582 DIMETHYL CHLOROFUMARATE



Beil. II - 744

 $\Pi_1$ -(302) $\Pi_2$ -(040)

B.P.

224°

(1)

 $D_4^{25} \text{ vac.} = 1.2800$  (2)

115.5° cor. at 18 mm. (2)

 $D_4^{20} = 1.300$  (3) $n_{D,16}^{20} = 1.471$  (3)

108° at 15 mm. (3)

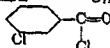
 $D_4^{17.0} = 1.3028$  (3) $n_{D,16}^{17.0} = 1.47108$  (3)

[For prepn. of  $\bar{C}$  from chlorofumaric acid (3:4853) in abs. MeOH with HCl gas (1) or conc.  $H_2SO_4$  (3) see indic. refs.; from chlorofumaryl (di)chloride (3:6165) with MeOH under reflux see (1).]

3:6582 (1) Kauder, *J. prakt. Chem.* (2) 31, 26-28, 32 (1885). (2) Walden, Swinne, *Z. physik. Chem.* 79, 741 (1912). (3) von Auwers, Harrea, *Ber.* 62, 1679, 1686-1687 (1929).

3:6500 *m*-CHLOROBENZOYL CHLORIDE

Beil. IX - 338

 $\text{IX}_1$ -(130)

B.P. 225°	(1)	(2)	143-145° at 40 mm.	(6)
224.8-228.2°	(3)		117.5° at 26 mm.	(7)
224-227°	(4)		112° at 21 mm.	(7)
222°	(5)		100.5° at 19 mm.	(7)
			103.5° at 15 mm.	(7)
			110° at 15 mm.	(8)
			103.4° at 12.5 mm.	(18)
			90.5° at 12.5 mm.	(7)
			91.5° at 10 mm.	(7)
			77.5-78° at 1 mm.	(9)

[For prepn. of  $\bar{C}$  from *m*-chlorobenzoic acid (3:4392) with  $PCl_5$  (76% yield (8)) (1) (5) or with  $SOCl_2$  (10) (6) see indic. refs.; from benzoyl chloride (3:6240) with  $Cl_2 + FeCl_3$  (83.5%  $\bar{C}$ ) see (7) (11); from tetrahydroxybenzoic acid [Beil. X-535,  $X_1$ -(276)] with 5 moles  $PCl_5$  see (12); from *o*-sulfobenzoic acid with 2 moles  $PCl_5$  see (1) (13).]

[Note that for the isomeric *p*-chlorobenzoyl chloride (3:6550) htg. with  $P_2O_5$  in toluene yields (16) the corresp. nnhydrides; although this reactn. is not recorded for  $\bar{C}$  yet the corresp. *m*-chlorobenzoic acid nnhydride, ndls. from alc. (17) or from lt. pet. (16), m.p. 95.5° (16), 05° (17), has been obtd. from *m*-chlorobenzoic acid (3:4392) with  $P_2O_5$  in boilg. toluene (30% yield (16)) or with oxalyl dichloride (3:5060) in boilg.  $C_6H_6$  (17).]

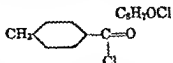
[ $\bar{C}$  with MeOH yields (5) methyl *m*-chlorobenzoate (3:6670), b.p. 231°;  $\bar{C}$  with EtOH yields (1) ethyl *m*-chlorobenzoate (3:6770), b.p. 245°.] [For studies of rate of alcoholysis of  $\bar{C}$  see (14) (9).]

[ $\bar{C}$  with  $C_6H_6 + AlCl_3$  gives (65% yield (6)) (2) (4) *m*-chlorobenzophenone (3:2160), m.p. 82-83°;  $\bar{C}$  with naphthalene +  $AlCl_3$  in  $CS_2$  gives (73% yield (15)) *m*-chlorophenyl  $\alpha$ -naphthyl ketone, pale yel. pr. from alc., m.p. 77-79° (15).]

$\bar{C}$  on hydrolysis (e.g., by boilg. with aq. (7)) yields *m*-chlorobenzoic acid (3:4392). For the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see *m*-chlorobenzoic acid (3:4392).

3:6590 (1) Limpricht, von Usler, *Ann.* 102, 262-263 (1857). (2) Hantzsch, *Ber.* 24, 57 (1891). (3) Kohlrausch, Pongratz, Stockmair, *Monatsh.* 67, 108 (1935). (4) Norris, Blake, *J. Am. Chem. Soc.* 50, 1812. (5) Montagne, *Rec. trav. chim.* 19, 55, 58 (1900). (6) Bergmann, Bondi, *Ber.* 64, 1477 (1931). (7) Hope, Riley, *J. Chem. Soc.* 121, 2510-2527 (1922). (8) Novello, Miriam, Sherwin, *J. Biol. Chem.* 67, 558 (1926). (9) Norris, Young, *J. Am. Chem. Soc.* 57, 1420-1424 (1935). (10) Frankland, Carter, Adams, *J. Chem. Soc.* 101, 2476-2477 (1912). (11) Hope, Riley, *J. Chem. Soc.* 123, 2470-2480 (1923). (12) Graebe, *Ann.* 138, 200-202 (1866). (13) Otto, *Ann.* 122, 156 (1862). (14) Berger, Olivier, *Rec. trav. chim.* 46, 516-527 (1927). (15) Scholl, Seer, *Ber.* 55, 113 (1922). (16) Rule, Paterson, *J. Chem. Soc.* 125, 2161 (1924). (17) Adams, Wirth, French, *J. Am. Chem. Soc.* 40, 427 (1919). (18) Thompson, Norris, *J. Am. Chem. Soc.* 58, 1956 (1936).

3:6600 *p*-TOLUYL CHLORIDE  
(*p*-Methylbenzoyl chloride)



Beil IX-486  
IX<sub>1</sub>-(193)

B.P.		F.P.			
225.5-226.7°	(1)	-3.9° (5)	$D_4^{20} = 1.1686$ (5)	$n_D^{20} = 1.5449$ (5)	
225-227°	(2)	-2.9° (6)			
224-226°	at 720 mm. (3)				
125°	at 36 mm. (14)				
101-102°	at 16 mm. (13)				
102°	at 15 mm. (4)				
102.7°	at 14 mm. (5)				
95-95.5°	at 10 mm. (6)				
72.8-73.0°	at 4.5 mm. (7)				
70-71°	at 4 mm. (8)				
90-90.5°	at 3 mm. (9)				

[For prepn. of  $\bar{C}$  from *p*-toluic acid (1:0795) with  $\text{PCl}_5$  (100% yield (3)) (6) (10), with  $\text{PCl}_5$  (11), with  $\text{SOCl}_2$  (95% yield (12)) (2) (7) (13) (14), with  $\text{POCl}_3 + \text{NaCl}$  (KCl) (15) see indic. refs.]

[ $\bar{C}$  with pyridine and excess  $\text{H}_2\text{S}_2\text{O}_5$  yields (16) *p*-toluic anhydride, m.p. 94° (also formed as by-product of prepn. of  $\bar{C}$  with  $\text{PCl}_5$  (6)).]

[For reactn. of  $\bar{C}$  with  $\text{AlCl}_3$  and various hydrocarbons to yield ketones, e.g., with  $\text{C}_6\text{H}_6$  yielding (3) phenyl *p*-tolyl ketone (1:5160), with toluene yielding (17) di-*p*-tolyl ketone (1:5185), with biphenyl yielding (18) (13) *p*-tolyl *p*'-xenyl ketone, with naphthalene yielding (19)  $\alpha$ -naphthyl *p*-tolyl ketone, with *m*-xylene yielding (14) *p*-tolyl *m*-xylyl ketone, with *p*-xylene yielding (14) *p*-tolyl *p*-xylyl ketone, with isopropylbenzene (cumene) yielding (20) *p*-cumyl *p*-tolyl ketone see indic. refs.]

[ $\bar{C}$  with  $\text{EtZnI}$  yields (21) ethyl *p*-tolyl ketone [Beil. VII-317, VII<sub>1</sub>-(170)], b.p. 238°.]

[ $\bar{C}$  with  $\text{Cl}_2$  at elevated temp yields (22) *p*-(chloromethyl)benzoyl chloride ( $\omega$ -chloro-*p*-toluyl chloride, b.p. 150-155° at 22 mm. (22);  $\bar{C}$  with  $\text{Br}_2$  at 185-190° yields (23) a mixt. of *p*-(bromomethyl)benzoyl chloride, b.p. 155-156° at 20 mm., and *p*-(bromomethyl)benzoyl bromide, b.p. 170-171° at 20 mm., m.p. 56° (23).]

[ $\bar{C}$  with  $\text{MeOH}$  yields methyl *p*-toluate (1:2071), m.p. 33°, b.p. 222.5°;  $\bar{C}$  with  $\text{EtOH}$  yields ethyl *p*-toluate (1:3917), b.p. 234.5°; for study of rate of reactn. with  $\text{MeOH}$  see (24), with  $\text{EtOH}$  see (9), with isopropyl alc see (25).]

$\bar{C}$  on hydrolysis yields *p*-toluic acid (1:0795), m.p. 176°; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see *p*-toluic acid (1:0795).

3:6600 (1) Kohlrausch, Pongratz, Stockmair, *Monatsh.* 67, 108 (1935). (2) Meyer, *Monatsh.* 22, 425 (1901). (3) Ador, Rulhet, *Ber.* 12, 2299-2299 (1879). (4) Frankland, Aston, *J. Chem.*

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(1896). (12) Maxim, *Bul. Soc. Chim.*

*nd.* 180, 1349-1351

*recr.* *Ann.* 394, 147

-1689 (1936); *Cent.*

1937, 1 2369; *C.A.* 31, 2591 (1937).

(21) Mauthner, *J. prakt. Chem.* (2) 103, 294 (1921/22). (22) Badische Anilin- und Soda-Fabrik, *Ger.* 239,311, Oct. 10, 1911; *Cent.* 1911, II 1394; *Ger.* 240,835, Nov. 15, 1911; *Cent.* 1911, II 1843. (23) Tittley, *J. Chem. Soc.* 1928, 2581. (24) Norris, Fasce, Staud, *J. Am. Chem. Soc.* 57, 1415-1420 (1935). (25) Norris, Gregory, *J. Am. Chem. Soc.* 50, 1813-1816 (1928).

# 4,6-DICHLORO-2-METHYLPHENOL

OH  $C_7H_6OCl_2$

Beil. VI - 359



VI<sub>1</sub>-(174)

VI<sub>2</sub>-(332)

B.P. 226.5°

M.P. 56°

See 3:1020. Division A: Solids.

# 3:6615 o-CHLOROACETOPHENONE (o-Chlorophenyl methyl ketone)



$C_8H_7OCl$

Beil. VII -

VII<sub>1</sub>-(151)

B.P.

228-229° at 758 mm. (10)

227-228° at 738 mm. (1)

226-228° (2)

220-222° (3)

113° at 18 mm. (4)

98° at 6 mm. (5)

$D_{25}^{25} = 1.1884$  (1)  $n_D^{25} = 1.686$  (1)

$D_{20}^{20} = 1.198$  (4)  $n_D^{20} = 1.5483$  (4)

$D_4^{15.5} = 1.2016$  (4)

Colorless mobile liquid with agreeable odor.

[For prepn. of  $\bar{C}$  from o-chlorophenyl-methyl-carbinol (4) (5) by oxidn. with  $CrO_3$  see (4) (5); from methyl o-chlorobenzoylacetate (60% yield (2)) or from ethyl o-chlorobenzoylacetate (80% yield (1)) (54% from  $\bar{C}$  (10)) on ketonic hydrol. with boilg. 20%  $H_2SO_4$  for 10-12 hrs. see indic. refs.; from o-chlorobenzonitrile [Beil. IX-336] with  $MeMgI$  in ether (56% yield) see (3).]

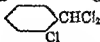
[ $\bar{C}$  with  $CuCN$  on hgt. in mixt. of quinoline + pyridine as directed (6) gives 20% yield o-cyanoacetophenone, m.p. 48°, b.p. 148° at 12 mm. (6); for behavior of  $\bar{C}$  on hgt. with  $CuCN$  in quinoline at 210° or with  $CuCN$  + phthalonitrile in quinoline yielding copper-contg. pigments of the phthalocyanine type see (7).]

[ $\bar{C}$  on hgt. with 50%  $KOH$  as directed (8) gives small yield o-chlorobenzoic acid.]

[ $\bar{C}$  on mononitration with 10 pts.  $HNO_3$  ( $D = 1.52$ ) at 0° gives (85% yield (1)) 2-chloro-4-nitroacetophenone, colorless pr. from alc., m.p. 62° (1) (for condens. of this prod. with arylamines to give substituted acridines see (9)).]

- ④ *o*-Chloroacetophenone oxime: ndls. from aq., m.p. 112-113° (4), 103° (1).  
 ⑤ *o*-Chloroacetophenone *p*-nitrophenylhydrazine: maroon cryst. from AcOH, m.p. 215° (2). (The phenylhydrazone of  $\bar{C}$  is unstable (2).)  
 ⑥ *o*-Chloroacetophenone 2,4-dinitrophenylhydrazine: dark yel. lfts. from AcOEt, m.p. 206° (3).  
 ⑦ *o*-Chloroacetophenone semicarbazone: cryst. from MeOH, m.p. 178-179° (3), from 40% AcOH, m.p. 159-160° (2).

3:6615 (1) Thorp, Brunskill, *J. Am. Chem. Soc.* 57, 1260-1261 (1915). (2) Wahl, Rolland, *Ann. chim.* (10) 10, 23-29 (1928). (3) Borsche, Scriba, *Ann.* 541, 290 (1939). (4) von Auwers, Lechner, Bundesmann, *Ber.* 58, 49-50 (1925). (5) Farbwerke Meister Lucius Brünig, Brit. 176,038, March 30, 1922; *Cent.* 1923, II 1252. (6) Helberger, von Rebay, *Ann.* 531, 283-284 (1937). (7) Helberger, *Ann.* 523, 216-217 (1937). (8) Lock, Böck, *Ber.* 70, 920 (1937). (9) Jensen, Rethwisch, *J. Am. Chem. Soc.* 56, 1145, 1149 (1938). (10) Sharp, Sutherland, Wilson, *J. Chem. Soc.* 1943, 346.

3:6625 *o*-CHLOROBENZAL (DI)CHLORIDE  $C_7H_4Cl_3$  Beil. V - 300  
 (*o*-Chlorobenzylidene (di)chloride)   $CHCl_2$   
 $Cl$   
 $V_1$ —  
 $V_2$ —

B.P. 228.5° (1)  $D_{15}^{15} = 1.399$  (1)  $n_D^{15} = 1.5670$  (4)  
 227-230° (2)  
 226-228° at 745 mm. (3)  
 100° at 10 mm. (3)

[For prepn of  $\bar{C}$  from *o*-chlorobenzaldehyde (3:6410) with  $PCl_5$  (86% yield (3)) (5) see indic. refs.; from *o*-toluenesulfonyl chloride with  $Cl_2$  at 92° (73.5% yield (4)) or at 150-200° (8) see indic. refs.; from *o*-chlorotoluene (3:8245) with  $Cl_2$  (1) in pres. of  $PCl_5$  at 150-180° (7) or in pres. of  $PCl_5$  at 102-105° (8) see indic. refs.; from *o*-hydroxybenzaldehyde (salicylaldehyde) (1:0205) with  $PCl_5$  see (2); for formn. of  $\bar{C}$  (5-7%) from benzal dichloride (3:6327) with  $Cl_2$  in pres. of  $I_2$  (accompanied by 43% *m*- and 46-47% *p*-isomers) see (9).]

[For use of  $\bar{C}$  in prepn. of triphenylmethane dyes see (10) (11); for condensation with isoviolanthrone in prepn. of vat dyes see (12).]

$\bar{C}$  on boilg. with water for 20 hrs. (3) or on htg. with aq. in s.t. at 170° (2) or with weakly fuming  $H_2SO_4$  at ord. temp. as directed (7) yields *o*-chlorobenzaldehyde (3:6410). [For studies of this hydrolysis under various other conditions see (13) (5).]

$\bar{C}$  on oxidn. with  $CrO_3$  (2), or  $\bar{C}$  on boilg. with aq. for 20 hrs. followed by treatment with cold conc. aq.  $KMnO_4$  (3), gives (75% yield (3)) *o*-chlorobenzoic acid (3:4159), m.p. 141° (3).

[ $\bar{C}$  in MeOH treated with molecular Ag + sand and htd. in s.t. for 6 hrs. at 95° yields (1)  $\alpha,\beta$ -dichloro- $\alpha,\beta$ -bis-(*o*-chlorophenyl)ethane [Beil. V-601], cryst. from ether + lgr., m.p. 170.5° (1)]

3:6625 (1) Gill, *Ber.* 26, 650-652 (1893). (2) Henry, *Ber.* 2, 136 (1869). (3) Asinger, Lock, *Monatsh.* 62, 333-334 (1933). (4) Davies, Duck, *J. Chem. Soc.* 1932, 2045. (5) Olivier, Weber, *Rec. trav. chim.* 53, 881, 888 (1934). (6) Gilliard, Monnet, Carlier, *Ger.* 98,433, Dec. 12, 1896, *Cent.* 1898, II 800. (7) Erdmann, *Ann.* 272, 151-152 (1892). (8) Kyrides (to National Aniline and Chem. Co.), U.S. 1,733,268, Oct. 29, 1929; *Cent.* 1930, I 3831. (9) Wertyporoch, *Ann.* 493, 161-162 (1932). (10) Geigy and Co., *Ger.* 213,503, Oct. 14, 1909; *Cent.* 1909, II 1515.

(11) Weller, Wenk, Stötter, *Ger.* 540,208, Dec. 12, 1931; *Cent.* 1932, I 3013. (12) Wuertz, Lycan (to du Pont Co.), U.S. 2,082,660, June 1, 1937; *Cent.* 1937, II 2077; *C.A.* 31, 5595 (1937). (13) Lock, Asinger, *Monatsh.* 59, 157-160 (1932).



## 3:6640 o-CHLOROBENZOYL CHLORIDE



Beil. IX - 336

IX<sub>1</sub>-(139)

B.P.		B.P. (cont.)		F.P. -4° (1)
229-230° at 773 mm.	(1)	114.5°	at 19.75 mm.	(15)
235-238°	(2)	110°	at 15 mm.	(8)
228-236° at 760 mm.	(3)	108°	at 14.5 mm.	(15)
233°	(4)	105°	at 12.75 mm.	(15)
227°	(11)	104.8-105.2°	at 12.5 mm.	(9)
224-224.5°	(5)	103.5°	at 12 mm.	(15)
224°	(6)	101.5°	at 11 mm.	(15)
137-139° at 60 mm.	(7)	93-95°	at 10 mm.	(7)
122° at 26.5 mm.	(15)	87°	at 9 mm.	(10)
		78.9-79.2°	at 2 mm.	(36)

[For prepn. of  $\bar{\text{C}}$  from o-chlorobenzoic acid (3:4150) with  $\text{PCl}_5$  (78% yield (11)) (2), with  $\text{PCl}_5 + \text{ZnCl}_2$  (78% yield (11)), with  $\text{SOCl}_2$  (yield: 00-98% (11), 87% (10)) (12) (13) (36), or with o-chlorobenzotrichloride (3:6830) +  $\text{ZnCl}_2$  (14) see indic. refs.; from o-chlorobenzaldehyde (3:6410) with  $\text{Cl}_2$  at 140-160° (70-72% yield) see (7); from toluene-o-sulfonyl chloride with  $\text{SOCl}_2$  in s.t. at 240° (41% yield) see (4).]

[For formn. of  $\bar{\text{C}}$  (together with other products) from benzoyl chloride (3:6240) with  $\text{Cl}_2 + \text{FeCl}_3$  (14.5%  $\bar{\text{C}}$ ) (15) (16), from o-hydroxybenzoic acid (salicylic acid) (1:0780) with  $\text{PCl}_5$  (17) (18) or with phosgene (3:5000) + pyridine in toluene at 60-80° (19); from sodium salicylate with  $\text{PCl}_5$  (18) (20); from o-sulfohenzoic acid dichloride by distn. at ord. press. (21) (8) (22) (3) see indic. refs.]

[ $\bar{\text{C}}$  with MeOH yields (1) methyl o-chlorobenzoate (3:6695) (for study of rate of reaction see (6));  $\bar{\text{C}}$  with EtOH yields (23) ethyl o-chlorobenzoate (3:6800) (for study of rate of reaction see (5)).]

[ $\bar{\text{C}}$  with Na o-chlorobenzoate should yield o-chlorobenzoic acid anhydride, ndls. from lt. pet. (25) or alc. (26), m.p. 79.6° (25), 78-79° (26); this anhydride also results from o-chlorobenzoic acid with  $\text{P}_2\text{O}_5$  in boilg. toluene (25) or with oxalyl dichloride (3:5060) in boilg.  $\text{C}_6\text{H}_6$  (26).]

[ $\bar{\text{C}}$  on cat. hydrogenation gives (70% yield (27)) (28) o-chlorobenzaldehyde (3:6410).]

[For reactn. of  $\bar{\text{C}}$  with  $\text{AlCl}_3 + \text{benzene}$  yielding (29) o-chlorobenzophenone (3:0715), with  $\text{AlCl}_3 + \text{o-chlorotoluene}$  yielding (30) 2,3-dichloro-4-methylbenzophenone, with  $\text{AlCl}_3 + \text{p-dichlorobenzene}$  yielding (31) 2,2',5',5'-trichlorobenzophenone, with  $\text{AlCl}_3 + \text{naphthalene}$  yielding (32)  $\alpha$ -naphthyl o-chlorophenyl ketone, or with anisole +  $\text{AlCl}_3$  (1:7445) yielding (33) 2-chloro-4-methoxybenzophenone see indic. refs.]

[For reactn. of  $\bar{\text{C}}$  with perylenetetracarboxylic acid diimide (34) or with aminodibenzanthrones (35) yielding vat dyes see indic. refs.]

$\bar{\text{C}}$  on hydrolysis yields o-chlorobenzoic acid (3:4150), m.p. 141°; for the amide, anilide, p-toluidide, and other derivs. corresp. to  $\bar{\text{C}}$  see o-chlorobenzoic acid (3:4150).

3:6640 (1) Montagne, *Rec. trav. chim.* 19, 55-56 (1900). (2) Emmerling, *Ber.* 8, 883 (1875). (3) Davies, Dick, *J. Chem. Soc.* 1932, 2044. (4) Pollak, Rudich, *Monatsh.* 43, 217-218 (1922). (5) Norris, Fasce, Staud, *J. Am. Chem. Soc.* 57, 1415-1420 (1935). (6) Norris, Young, *J. Am. Chem. Soc.* 57, 1420-1424 (1935). (7) Clarke, Taylor, *Org. Syntheses*, Coll. Vol. 1 (2nd ed.), 155-156 (1941); (1st ed.), 148-149 (1932); 9, 34-35 (1929). (8) Fritsch, *Ber.* 29, 2299 (1896). (9) Kohlrausch, Pongratz, Stockmair, *Monatsh.* 67, 108 (1935). (10) Novello, Miriam, Sherwin, *J. Biol. Chem.* 67, 557 (1926).

(11) Clark, Bell, *Trans. Roy. Soc. Can.* (3) 27, III 97-103 (1933). (12) Frankland, Carter, Adams, *J. Chem. Soc.* 101, 2476 (1912). (13) Meyer, *Monatsh.* 22, 427 (1901). (14) Scottish Dyes, Ltd., Bangham, Thomas, *Brit.* 308,231, April 18, 1929, *Cent.* 1929, II 1348; *C.A.* 24, 129 (1930). (15) Hope, Riley, *J. Chem. Soc.* 121, 2510-2527 (1922). (16) Hope, Riley, *J. Chem. Soc.*, *Ann.* 83, 317-318 (1852). (17) Kolbe, Lautermann, *em. Ind. Basel, Brit.* 401,643, Dec. 14, 1933; *Cent.* 1934, I 287. (18) Reichenbach, Beilstein, *Ann.*

132, 311-313 (1864).

(21) Remsen, Kohler, *Am. Chem. J.* 17, 332-333 (1895). (22) List, Stein, *Ber.* 31, 1653-1654 (1898). (23) Kekulé, *Ann.* 117, 153-154 (1861). (24) Berger, Olivier, *Rec. trav. chim.* 46, 516-527 (1927). (25) Rule, Paterson, *J. Chem. Soc.* 125, 2161 (1924). (26) Adams, Wirth, *J. Am. Chem. Soc.* 40, 127 (1918). (27) Doering, Zetzsche, *Ber.* 54, 125-127 (1921).

### 2,3,4-TRICHLOROTOLUENE


 $C_7H_5Cl_3$ 

Beil. V - 298

V<sub>1</sub>—

V<sub>2</sub>-(232)

B.P. 231-232° at 716 mm.

M.P. 41°

See 3:0425. Division A. Solids.

### 2,3,5-TRICHLOROTOLUENE


 $C_7H_5Cl_3$ 

Beil. V - 299

V<sub>1</sub>—

V<sub>2</sub>—

B.P. 229-231° at 757 mm.

M.P. 45-46°

See 3:0610. Division A. Solids.

### 2,4,5-TRICHLOROTOLUENE


 $C_7H_5Cl_3$ 

Beil. V - 299

V<sub>1</sub>-(152)

V<sub>2</sub>-(232)

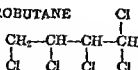
B.P. 229-230° at 716 mm.

M.P. 82°

See 3:2100. Division A. Solids.

### 1,1,2,3,4-PENTACHLOROBUTANE

(Solid diastereoisomer)


 $C_4HCl_5$ 

Beil. S.N. 10

B.P. 230°

M.P. 49°

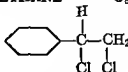
$D_D^{53} = 1.539$

$n_D^{53} = 1.5065$

See 3:0750. Division A. Solids.

3:6685 *d,l*-1,2-DICHLORO-1-PHENYLETHANE

Beil. V - 354

*(α,β*-Dichloroethylbenzene;  
styrene dichloride) $V_1$ — $V_2$ -(278)

B.P.

233-234° at 759 mm. (1)

 $D_4^{15} = 1.240$  (1) $n_D^{15} = 1.5544$  (1)

114.5-115.5° at 15 mm. (1)

93° at 5 mm. (2)

Limpid liq. with faint odor.

[For prepn. of  $\bar{C}$  from phenylethylene (styrene) (1:7435) with  $Cl_2$  in  $CHCl_3$  at 0° (1) cf. (3) or in  $CCl_4$  at 40-50° (4) (note that some  $\beta$ -chlorostyrene (3:8717) is also formed (4)) see indic. refs.; for formn. of  $\bar{C}$  in reaction of styrene (1:7435) with  $NCl_3$  in  $CCl_4$  at -10° (5) or from ethylbenzene (1:7410) with  $Cl_2$  in bright sunlight (6) see indic. refs.]

[ $\bar{C}$  with a mildly alkaline agent such as  $Na_2CO_3$ ,  $NaOAc$ ,  $CaO$ , or  $CaCO_3$  (but not alkali hydroxide) as directed (7) undergoes hydrolysis of its  $\alpha$ -chlorine atom giving chloromethyl-phenyl-carbinol (styrene chlorohydrin) (3:9570).]

[ $\bar{C}$  passed over activated  $Al_2O_3$  at 360-400° and 85-105 mm. pres. (4) or  $\bar{C}$  with pyridine as directed (8) loses  $HCl$  giving (92% yield (4))  $\beta$ -chlorostyrene (3:8717).]

[ $\bar{C}$  with aq. alc.  $NaOH$  at 50-60° for 4 hrs. loses  $HCl$  (in the opposite sense from preceding paragraph) giving (80% yield (4))  $\alpha$ -chlorostyrene (3:8715).]

3:6685 (1) Biltz, *Ann.* 296, 275-277 (1897). (2) Knorr (to I.G.), *Ger.* 559,521, Sept. 21, 1932; *Cent.* 1933, I 1843; *C.A.* 27, 736 (1933); French 735,000, Oct. 31, 1932; *Cent.* 1933, I 1843, *C.A.* 27, 1011 (1933). (3) Blyth, Hofmann, *Ann.* 53, 309-310 (1845). (4) Emerson, Agoew, *J. Am. Chem. Soc.* 67, 518-520 (1945). (5) Coleman, Campbell, *J. Am. Chem. Soc.* 50, 2754-2755 (1928). (6) Evans, Mabbott, Turner, *J. Chem. Soc.* 1927, 1163. (7) I.G., French 735,103, Nov. 3, 1932; *Cent.* 1933, II 1093; *C.A.* 27, 1011 (1933). (8) I.G., French 729,730, July 30, 1932; *Cent.* 1933, II 3015; *C.A.* 27, 307 (1933).

3:6695 METHYL *o*-CHLOROBENZOATE

Beil. IX - 336

 $IX_1$ —

B.P. 234-235° at 762.4 mm. (1)

233-236° ] at 760 mm. (8)

229-230° (2)

119.5-120.5 at 24.4 mm. (3)

119° at 19 mm. (4)

111-113° at 14 mm. (8)

113-115° at 11 mm. (5)

 $n_D^{22} = 1.535$  (8)

[For prepn. of  $\bar{C}$  from *o*-chlorobenzoic acid (3:4150) with  $MeOH + HCl$  (2) or  $MeOH + H_2SO_4$  (2) (5) or  $MeOH + BF_3 \cdot Et_2O$  (70.6% yield (4)) see indic. refs.; from *o*-chlorobenzoyl chloride (3:6640) with  $MeOH$  see (1).]

$\bar{C}$  on htg. with sirupy  $H_3PO_4$  at 200° yields (6) *o*-chlorobenzoic acid (3:4150), chlorobenzene (3:7903), dimethyl ether +  $CO_2$ .

$\bar{C}$  added to 5-6 pts. very conc.  $HNO_3$  at 0°, poured onto ice, yields (1) mainly methyl 2-chloro-5-nitrobenzoate [Beil. IX-403], ndls. from  $MeOH$ , m.p. 73° (1).

[ $\bar{C}$  with  $Na +$  methyl acetate condenses giving (65-70% yield (5)) methyl *o*-chlorobenzoylacetate, b.p. 170-172° at 12 mm. (5); this prod. with excess phenylhydrazine in

alc. + AcOH gives on htg. 3-(*o*-chlorophenyl)-1-phenylpyrazolone-5, colorless ndls. from MeOH, m.p. 113-114° (5); corresp. prod. from *p*-nitrophenylhydrazine, m.p. 203-204° (5).]

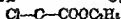
$\bar{C}$  on hydrolysis (Sap. Eq. = 170.5) yields methyl alcohol (1:6120) + *o*-chlorobenzoic acid (3:4150). [For studies of hydrolysis under various cond. see (2) (3) (7).] — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see *o*-chlorobenzoic acid (3:4150).

Chem. Soc. 123, 2695-2697 (1923); 125, 2593-2594 (1924). (8) Kahovec, Wagner, *Monatsh.* 74, 284 (1943).  
 las, *Z. physik. Chem.* 24, 10, 9-13, 17-18 (1928).  
 ombie, Scarborough, *J.*

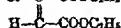
### 3:6697 DIETHYL CHLOROMALEATE



Beil. II - 753



II<sub>1</sub>-(305)



II<sub>2</sub>-(646)

B.P.

235° at 760 mm., sl. dec. (1)  $D_4^{25} \text{ vac.} = 1.1914$  (2)

189.5-190.5° at 210 mm. (1)

125.5° cor. at 19 mm. (2)  $D_4^{20} = 1.174$  (4) (5)  $n_D^{20} = 1.455$  (4)

122° at 15 mm. (3) 1.4549 (5)

120° at 12 mm. (5)

$D_4^{19} = 1.1754$  (4)  $n_D^{19} = 1.45532$  (4)

[See also diethyl chlorofumarate (3:6864).]

Colorless oil with pleasant odor.

[For prepn. of  $\bar{C}$  from chloromaleic anhydride (3:0280) in abs. EtOH with conc.  $H_2SO_4$  in cold (4) or on refluxing several hrs. (6) or from silver salt of chloromaleic acid (3:3432) with EtI (1) (3) see indic. refs.]

[ $\bar{C}$  (1 mole) with ethyl sodioacetoacetate (1 mole) in abs. alc. refluxed  $\frac{1}{2}$  hr. reacts readily yielding (3) (7) triethyl  $\gamma$ -acetylaconitate (Beil. III-860), yel. oil, b.p. 187-188° at 15 mm. (3), the same prod. as similarly obtd. from diethyl chlorofumarate (3:6864).]

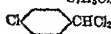
[ $\bar{C}$  with 6% alc.  $NH_3$  (2 moles) at ord. temp. for 5-6 days reacts to yield (6) diethyl iminosuccinate (diethyl aminoohuten-2-dioate) (Beil. III-784), b.p. 144-145° at 25 mm. (6), identical with the prod. from similar treatment of the isomeric diethyl chlorofumarate (3:6864) q.v.]

3:6697 (1) Perkin, *J. Chem. Soc.* 53, 708 (1889). (2) Walden, Swinne, *Z. physik. Chem.* 79, 742 (1896). (4) von Auwers, Harres, *physik. Chem.* A-143, 10 (1929). (6) Ruhemann, *J. Chem. Soc.* 71, 323-324 (1897).

### 3:6700 *p*-CHLOROBENZAL (DI)CHLORIDE (*p*-Chlorobenzylidene dichloride)



Beil. V - 300



V<sub>1</sub>—

V<sub>2</sub>-(232)

B.P. 236° at 755 mm. (1)

234° (2)

127-132° at 22 mm. (3)

108° at 10 mm. (1)

[For prepn. of  $\bar{C}$  from *p*-chlorobenzaldehyde (3:0765) with  $PCl_5$  see (1) (4); from *p*-toluenesulfonyl chloride with  $SOCl_2$  in a.t. at  $140^\circ$  for 18 hrs. (54% yield (3)) or with  $Cl_2$  at  $150-200^\circ$  (accompanied by *p*-chlorobenzotrichloride, (3:6825) (5)) see indic. refs.; for formn. of  $\bar{C}$  (47% (6)) from benzal dichloride (3:6327) with  $Cl_2$  in pres. of  $I_2$  (6) (2) (accompanied by 5-7% *o*- and 43% *m*-isomers (6)) see indic. refs.]

[For use of  $\bar{C}$  in prepn. of triphenylmethane dyes see (7).]

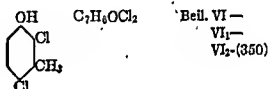
$\bar{C}$  on refluxing with aq. for 20 hrs. (1) or on htg. with aq. in a.t. at  $170^\circ$  (2) yields *p*-chlorobenzaldehyde (3:0765). [For studies of this hydrolysis under various other conditions see (4) (1).]

$\bar{C}$  on oxidn. with  $CrO_3$  (2), or  $\bar{C}$  on refluxing with aq. for 20 hrs. followed by treatment with cold conc. aq.  $KMnO_4$  (1), gives (85% yield (1)) *p*-chlorobenzoic acid (3:4940), m.p.  $240^\circ$  (1).

[For behavior of  $\bar{C}$  with  $MeMgCl$  see (8).]

3:6700 (1) Asinger, Lock, *Monatsh.* 62, 336 (1933). (2) Beilsteio, Kuhlberg, *Ann.* 146, 327-329 (1868). (3) Pollak, *F.* 53, 881, 888 (1934). (6) Wertyporoch, *Ann.* 1931; *Cent.* 1932, I 30

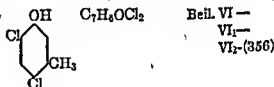
— 2,4-DICHLORO-3-METHYLPHENOL



B.P.  $235-236^\circ$  at 745 mm. M.P.  $58-59^\circ$

See 3:1205. Division A: Solids.

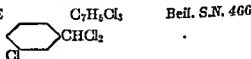
— 4,6-DICHLORO-3-METHYLPHENOL



B.P.  $235-236^\circ$  M.P.  $71-72^\circ$

See 3:1745. Division A: Solids.

3:6710 *m*-CHLOROBENZAL (DI)CHLORIDE  
(*m*-Chlorobenzylidene dichloride)



B.P.  $235-237^\circ$  at 738 mm. (1)  
 $105^\circ$  at 11 mm. (1)

Colorless liq. with agreeable odor.

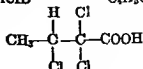
[For prepn. of  $\bar{C}$  from *m*-chlorobenzaldehyde (3:6475) with  $PCl_5$  (75% yield (1)) (2) see indic. refs.; for formn. of  $\bar{C}$  from benzal dichloride (3:6327) with  $Cl_2$  in pres. of  $I_2$  (43%  $\bar{C}$  together with 5-7% *o*- and 46% *p*-isomers) see (3).]

$\bar{C}$  on refluxing 20 hrs. with aq. then treated in cold with conc. aq.  $KMnO_4$  gives (70% yield (1)) *m*-chlorobenzoic acid (3:4392), m.p.  $155^\circ$  (1).]

3:6710 (1) Asinger, Lock, *Monatsh.* 62, 334-336 (1933). (2) Olivier, Weber, *Rec. trav. chim.* 53, 882, 888 (1934). (3) Wertyporoch, *Ann.* 493, 161-162 (1932).

—  $\alpha,\alpha,\beta$ -TRICHLORO-*n*-BUTYRIC ACID

Beil. II - 280

 $\Pi_1$ -(124) $\Pi_2$ -(255)

B.P. 236-238°

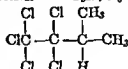
M.P. 60°

See 3:1280. Division A: Solids.

## 3:6725 3,3,4,4,4-PENTACHLORO-2-METHYLBUTANE



Beil. I - 136

 $I_1$ — $I_2$ —

B.P. 235-240° (1)

[For propn. of  $\bar{C}$  from diisocamyl sulfide [Beil. I-405,  $I_1$ -(200),  $I_2$ -(435)] by actn. of  $Cl_2$  see (1).]

$\bar{C}$  on htg. 7 hrs. at 110° in a s.t. with  $Ag_2O$  and aq. yields (1)  $CO_2$  + isobutyric acid (1:1030) (as  $Ag\bar{A}$ ).

3:6725 (1) Spring, Lecrenier, *Bull. soc. chim.* (2) 48, 627-628 (1887).

## — 3,5-DICHLOROBENZALDEHYDE



Beil. S.N. 635



B.P. 235-240° at 748 mm.

M.P. 65°

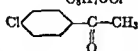
See 3:1475. Division A: Solids.

3:6735 *p*-CHLOROACETOPHENONE

(p-Chlorophenyl methyl ketone)



Beil. VII - 281

 $VII_1$ -(151)

B.P.

M.P.

236.5°

cor. at 740 mm. (1)

20.5°

(10) (11) (12)

 $D_4^{20} = 1.188$  (2)

232°

(3)

20-21°

(5) (1)

231-232°

(4) (17)

20°

(2)

124-126°

at 24 mm. (5)

10.8°

(13)

113°

at 14 mm. (3)

10°

(14)

108-111°

at 13 mm. (6)

17.6-17.8°

(15)

152°

at 12 mm. (7)

00°

at 7 mm. (1)

80.4-91°

at 5 mm. (8)

Insol. aq.; misc. alc. or ether. —  $\bar{C}$  does not yield an addo. prod. with  $NaHSO_4$ .

[For propn. of  $\bar{C}$  from chlorobenzene (3:7903) with  $Ac_2O$  +  $AlCl_3$  in  $CS_2$  (yields: 83-79% (15), 78-74% (5), 68-66% (1)) (5) (9) or with acetyl chloride (3:7065) +  $AlCl_3$  in absence

of solvent (poor yield (2)) or in  $\text{CS}_2$  (yields: 80–90% (16), 81% (6), 41% (17)) see indie. refs.; from *p*-chlorobenzoylacetic acid on warming (18); from methyl *p*-chlorobenzoylacetic acid (4) on ketonic hydrolytic cleavage by boilg. 10–12 hrs. with 20%  $\text{H}_2\text{SO}_4$  see (4).]

[ $\bar{\text{C}}$  in  $\text{CS}_2$  treated with 1 mole  $\text{Cl}_2$  yields (19) *p*-chlorophenacyl chloride (3:2990), m.p. 101°;  $\bar{\text{C}}$  with 2 moles  $\text{Cl}_2$  at 50–60° without solv. (19) yields 4,  $\omega$ ,  $\omega$ -trichloroacetophenone [Beil. VII-283], m.p. 57°. —  $\bar{\text{C}}$  with 1 mole  $\text{Br}_2$  in  $\text{CS}_2$  or  $\text{AcOH}$  yields (17) (20) *p*-chlorophenacyl bromide [Beil. VII-285], cryst. from alc., m.p. 96.5° (20), 96° (17) (for studies of rate of bromination see (13), of influence of light and other factors see (21));  $\bar{\text{C}}$  with excess  $\text{Br}_2$  directly (22), in  $\text{AcOH}$  (17), or in  $\text{CCl}_4$  susp. of  $\text{CaCO}_3$  (22) yields 4-chloro- $\omega$ ,  $\omega$ -dibromoacetophenone [Beil. VII-286], m.p. 93.5–94.5° (22), 92.5° (17).] [Note proximity of this m.p. to that (96°) of *p*-chlorophenacyl bromide (above).]

[ $\bar{\text{C}}$  on mononitration with mixt. of conc.  $\text{HNO}_3$  + conc.  $\text{H}_2\text{SO}_4$  at  $-10^\circ$  as directed (6) or added slowly to 10 pts.  $\text{HNO}_3$  ( $D = 1.5$ ) at 0° (23) yields 4-chloro-3-nitroacetophenone, ndls. from alc., m.p. 104° (6), 99–101° (23) (accompanied in the former case (6) by a little 4-chloro-3-nitrobenzoic acid, m.p. 181°).]

$\bar{\text{C}}$  in alk. medium readily condenses with aldehydes: e.g.,  $\bar{\text{C}}$  in dil. alc. with a little alk. gives (yields: 96% (24), 93% (25), 83% (7)) henzal *p*-chloroacetophenone (*p*-chloro-chalcone), cryst. from ether of  $\text{CHCl}_3$ , m.p. 101° (24), 98.5° (7), 96.4° (12), 96° (25) (for study of rate of condensation see (12)); similarly  $\bar{\text{C}}$  with salicylaldehyde (1:0205) yields (23) salicylidene-*p*-chloroacetophenone, yel. ndls. from alc., m.p. 151° (23);  $\bar{\text{C}}$  with *p*-dimethylaminobenzaldehyde yields (26) *p*-dimethylaminobenzal-*p*-chloroacetophenone, yel. ndls. from alc., m.p. 140–140.5° (26); for corresp. condensation of  $\bar{\text{C}}$  with *p*-chlorobenzaldehyde (3:0765) see (16), with *o*-nitrobenzaldehyde see (27) (28).

[ $\bar{\text{C}}$  also readily condenses with esters: e.g.,  $\bar{\text{C}}$  in abs. alc. +  $\text{NaOEt}$  treated with ethyl formate (1:3000) gives (28) hydroxymethylene-*p*-chloroacetophenone, yel. ndls. from pet. eth., m.p. 48–49° (28);  $\bar{\text{C}}$  with ethyl phenylacetate (1:3872) in ether with  $\text{Na}$  gives (40% yield (29))  $\omega$ -(phenylacetyl)-*p*-chloroacetophenone.]

[ $\bar{\text{C}}$  with  $\text{PCl}_5$  at 100° for 4 hrs. gives (60% yield (30)) *p*,  $\alpha$ -dichlorostyrene, b.p. 115–116° at 20 mm., m.p.  $-6$  to  $-5^\circ$ ,  $D_{25}^{25} = 1.247$ ,  $n_D^{25} = 1.5735$  (30);  $\bar{\text{C}}$  with selenium oxychloride ( $\text{SeOCl}_2$ ) gives (50% yield (31)) *bis*-(*p*-chlorophenacyl)selenium dichloride, m.p. 126° (31);  $\bar{\text{C}}$  with  $\text{K}$  pyrosulfate + a little conc.  $\text{H}_2\text{SO}_4$  htd. at 80° for 4 hrs. (46% yield (32)) or  $\bar{\text{C}}$  with 1%  $\text{I}_2$  htd. 4 hrs. at 170° (32) gives 1,3,5-*tris*-(*p*-chlorophenyl)benzene, white ndls. from  $\text{AcOEt}$ , m.p. 238° (32); for behavior of  $\bar{\text{C}}$  with  $\text{NOCl}$  see (33) (14), with  $\text{NaOEt}$  + amyl nitrite in alc. see (34) (35).]

[ $\bar{\text{C}}$  htd. as directed with excess  $\text{NH}_4$  formate and the intermediate formyl deriv. hydrolyzed with  $\text{HCl}$  gives (yields: 82% (36), 65% (37)) *d,l*- $\alpha$ -(*p*-chlorophenyl)ethylamine, b.p. 105° at 10 mm.,  $D_{20}^{20} = 1.1178$ ,  $n_D^{25} = 1.5420$  (hydrochloride, m.p. 192–193°, *N*-henzoyl deriv., m.p. 144–145° (36)).]

[ $\bar{\text{C}}$  on htg. with 10% aq.  $\text{NaOH}$  +  $\text{Cu}$  at 190° for 5 hrs. under press. yields (38) *p*-hydroxyacetophenone (1:1527), m.p. 109°;  $\bar{\text{C}}$  with conc. aq.  $\text{NH}_4\text{OH}$  in pres. of  $\text{Cu}_2\text{O}$  htd. 5 hrs. at 220° under press. yields (39) *p*-aminoacetophenone [Beil. XIV-46, XIV-1-(366)];  $\bar{\text{C}}$  on htg. with 50%  $\text{KOH}$  as directed (40) gives small yield of *p*-chlorobenzoic acid (3:4940);  $\bar{\text{C}}$  with alc.  $\text{NaOEt}$  htd. in s.t. at 130°–140° gives (41) *p*-chlorophenyl-methyl-carbinol, *p*-chlorobenzoic acid, and other prods.]

$\bar{\text{C}}$  on oxidn. with  $\text{KMnO}_4$  (2) or in  $\text{MeOH}$  soln. with  $\text{NaOH}$  +  $\text{Cl}_2$  (93% yield (42)) or with  $\text{CrO}_3$  +  $\text{H}_2\text{SO}_4$  (95% yield (43)) or by cat. vapor-phase oxidn. (90% yield (44)) gives *p*-chlorobenzoic acid (3:4940), m.p. 242°. [Note that  $\bar{\text{C}}$  in abs. alc. refluxed with  $\text{SeO}_2$  gives (45) *p*-chlorophenylglyoxal, m.p. 122° (for study of rate see (46)).]

⑩ *p*-Chloroacetophenone oxime: ndls. from alc., m.p. 95° (17). [This prod. with conc.

$H_2SO_4$  htd. at  $100^\circ$  rearranges to acet-*p*-chloroanilide [Beil. XII-611, XII<sub>1</sub>-(306)], m.p.  $172-173^\circ$  (17).]

③ *p*-Chloroacetophenone phenylhydrazone: m.p.  $114^\circ$  (17),  $112-113^\circ$  (48) (decomposes on stdg. 2 days (17) (4).)

④ *p*-Chloroacetophenone *p*-nitrophenylhydrazone: maroon cryst. from AcOH, m.p.  $239^\circ$  (4).

⑤ *p*-Chloroacetophenone 2,4-dinitrophenylhydrazone: scarlet cryst., m.p.  $231^\circ$  cor. (47).

⑥ *p*-Chloroacetophenone semicarbazone: white cryst. from 40% AcOH, m.p.  $200-201^\circ$  (4).

3:6735 (1) Noller, Adams, *J. Am. Chem. Soc.* 46, 1893 (1924). (2) Gautier, *Ann. chim.* (6) 14, 372-375 (1888). (3) Kahovec, Wagner, *Proc. Indian Acad. Sci. A-8*, 325 (1938). (4) Wahl, Rolland, *Ann. chim.* (10) 10, 27-31, 34-35 (1925). (5) Adams, Noller, *Org. Syntheses*, Coll. Vol. 1 (2nd ed.), 111 (1941), (1st ed.), 105 (1932), 5, 19 (1925). (6) Mayer, Stark, Schön, *Ber.* 65, 1334 (1932). (7) Bergmann, Hampson, *J. Chem. Soc.* 1935, 991. (8) Groggins, U.S., 1,991,743, Feb. 19, 1935; *Cent.* 1936, I 583, C.A. 29, 2175 (1935). (9) Groggins, U.S. 2,008,418, July 16, 1935; *Cent.* 1936, I 1500; C.A. 29, 5856 (1935). (10) Hassel, Naeshagen, *Z. physik. Chem. B-15*, 419 (1932).

(11) Evans, Morgan, Watson, *J. Chem. Soc.* 1935, 1172. (12) Coombs, Evans, *J. Chem. Soc.* 1940, 1295 (13) Nathan, Watson, *J. Chem. Soc.* 1933, 220. (14) Edkins, Linnell, *Quart. J. Chem. Soc.* 1917, 1262 (1915). (19) Ref. 2, pp. 395-396, 402. (20) Judefind, Reid, *J. Am. Chem. Soc.* 42, 1044-1045 (1920).

(21) Sampey, Illicks, *J. Am. Chem. Soc.* 63, 1098-1101 (1941). (22) Fisher, *J. Am. Chem. Soc.* 53, 4895 (1933). (23) G. G. LeFèvre, R. J. W. LeFèvre, *J. Chem. Soc.* 1932, 1989-1992. (24) Diltney, *J. prakt. Chem.* (2) 101, 199 (1920). (25) Allen, Frame, *Can. J. Research* 6, 605-613 (1932), *Cent.* 1932, II 3880; C.A. 26, 5086 (1932). (26) Fleiffer, Kleu, *Ber.* 66, 1706 (1933). (27) Tanasescu, Baci, *Bull. soc. chim.* (5) 4, 1748-1749; 1677-1678 (1937) (28) Benary, *Ber.* 61, 2253 (1928). (29) Kohler, Smith, *J. Am. Chem. Soc.* 44, 630 (1922). (30) Vaughn, Nieuwland, *J. Am. Chem. Soc.* 56, 1208 (1934).

(31) Nelson, Jones, *J. Am. Chem. Soc.* 52, 1589 (1930). (32) Bernhauer, *J. prakt. Chem.* (2) 145, 305 (1930). (33) Rheinboldt, Schmitz-Dumont, *Ann.* 444, 129 (1925). (34) Avogadro, (35) Ingersoll, Brown, Ingersoll, *Org. Syntheses*, 2nd. Co., U.S. 1,961,630, Bryner (to Dow Chem. 934). (40) Lork, Bäck, *Ber.* 70, 921 (1937).

(41) Gastaldi, Cherchi, *Gazz. chim. Ital* 45, II 271-273 (1915). (42) von Arendonk, Cupery, *id. Eng. Chem.* 27, 1397 (43) Karrer, Musante, *Gen. Chem. (U.S.S.R.) Org. Chem.* 2, 224 (1935).

3:6750 ETHYL *p*-CHLOROBENZOATE

$C_9H_9O_2Cl$

Beil. IX - 340

IX<sub>1</sub>-(140)

B.P.

238°

(1)

237.4-238.0°

(2)

142°

at 50 mm.

(3)

121-122°

at 16 mm.

(4)

122°

at 15 mm.

(5)

120.1-120.2°

at 15 mm.

(2)

118°

at 15 mm.


(6)

118°

at 14 mm.

(7)

Cl



COOC<sub>2</sub>H<sub>5</sub>

$D_4^{110} = 1.1873$

(8)

$n_D^{14} = 1.52700$

(9)



[For prepn. of  $\bar{C}$  from *p*-chlorobenzoic acid (3:4940) with EtOH + H<sub>2</sub>SO<sub>4</sub> see (1) (3); from *p*-chlorobenzoyl chloride (3:6550) with abs. EtOH see (2).]

$\bar{C}$  in alc. soln. on htg. with hydrazine hydrate yields (9) (10) *p*-chlorobenzhydrazide, white ndls. from alc., m.p. 162–163° (10). [This prod. with BzH yields benzal *p*-chlorobenzhydrazide, ndls. from 95% alc., m.p. 227–229° (10).] [For use of *p*-chlorobenzhydrazide as reagt. for identification of aldehydes and ketones see (10).]

$\bar{C}$  (1.5 moles) with NaOEt (0.3 mole) at 160–180° for 1 hr. gives (75% yield (15)) di- (*p*-chlorobenzoyl)methane, cryst. from MeOH, m.p. 158–159° (15).]

$\bar{C}$  on hydrolysis (Sap. Eq. = 184.6) yields ethyl alcohol (1:6130) + *p*-chlorobenzoic acid (3:4940). [For studies of hydrolysis of  $\bar{C}$  under various conditions see (7) (6) (11) (4) (12) (5) (13) (14).] For the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see *p*-chlorobenzoic acid (3:4940).

3:6750 (1) van Raalte, *Rec. trav. chim.* 18, 398 (1899). (2) Kohlrausch, Stockmair, *Monatsh.* 66, 325 (1935). (3) Bergmann, Engel, *Z. physik. Chem.* B-15, 95 (1932). (4) Kindler, *Ann.* 450, 16 (1926). (5) Timm, Hinshelwood, *J. Chem. Soc.* 1938, 866–869. (6) Cashmore, McCombie, Scarborough, *J. Chem. Soc.* 121, 243–253 (1922). (7) McCombie, Scarborough, *J. Chem. Soc.* 107, 159 (1915). (8) von Auwers, *Ann.* 422, 166 (1921). (9) Kahl, *Cent.* 1904, II 1493. (10) Shih, *Sab. Science Repts. Nall, Tsing-Hua Univ.* A-2, 353–357 (1934); *Cent.* 1935, I 50–57; *C.A.* 29, 466 (1935).

(11) McCombie, Scarborough, Settle, *J. Chem. Soc.* 121, 2308–2318 (1922). (12) Blakey, McCombie, Scarborough, *J. Chem. Soc.* 1926, 2867. (13) Westheimer, *J. Am. Chem. Soc.* 62, 1893 (1940). (14) Price, Westheimer, *J. Chem. Phys.* 11, 150–153 (1943). (15) McElvain, Weber, *J. Am. Chem. Soc.* 63, 2196 (1941).

— *o*-XYLYLENE (DI)CHLORIDE



Beil. V - 364

V<sub>1</sub>—

V<sub>2</sub>-(283)

B.P. 239–241°

M.P. 55°

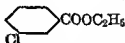
See 3:1040. Division A: Solids.

3:6770 ETHYL *m*-CHLOROBENZOATE



Beil. IX - 337

IX<sub>1</sub>-(139)



B.P.

[245° (1)]

$D_4^{15.4} = 1.1859$  (7)

$n_D^{15.4} = 1.52233$  (7)

239.3–241.7° (2)

130.0–130.5° at 20–21 mm. (3)

124° at 21.5 mm. (4)

121° at 20 mm. (5)

114.6–116.2° at 16 mm. (2)

119° at 13 mm. (6)

[For prepn. of  $\bar{C}$  from *m*-chlorobenzoic acid (3:4392) with EtOH + H<sub>2</sub>SO<sub>4</sub> (1) or with 5% EtOH/HCl (90% yield (8)) see indic. refs.; from *m*-chlorobenzoyl chloride (3:6590) with EtOH see (1) (2).]

$\bar{C}$  on electrolytic reductn. in alc./H<sub>2</sub>SO<sub>4</sub> soln. yields (9) *m*-chlorobenzyl ethyl ether [Beil. VI-444], b.p. 219° (9).]

$\bar{C}$  on refluxing with hydrazine hydrate gives (97% yield (8)) *m*-chlorobenzhydrazide, ndls. from aq. or alc., m.p. 158° (8), 157–158° (10). [This prod. in aq. soln. on htg. with BzH + a few drops AcOH yields benzal-*m*-chlorobenzhydrazide, floccs from alc., m.p. 118°

(8) (10).] [For study of prepn. and use of *m*-chlorobenzhydrazide as reagent for identification of aldehydes and ketones see (10).]

$\bar{C}$  on hydrolysis (Sap. Eq. = 184.5) yields ethyl alcohol (1:6130) + *m*-chlorobenzoic acid (3:4392). [For studies of hydrolysis of  $\bar{C}$  under various conditions see (6) (11) (5).] — For the amide, anilide, *p*-toluidide, and other derivatives corresp. to  $\bar{C}$  see *m*-chlorobenzoic acid (3:4392).

3:6770 (1) Limpicht, von Usler, *Ann.* 102, 262 (1857). (2) Kohlrausch, Stockmair, *Monatsh.* 66, 324 (1935). (3) Kindler, *Ann.* 450, 17 (1926). (4) Curtius, Melzbach, *J. prakt. Chem.* (2) 81, 536 (1910). (5) Evans, Gordon, Watson, *J. Chem. Soc.* 1937, 1430-1432. (6) McCombie, *J. Chem. Soc.* 1926, 2867. (7) von Auwers, *Ann.* 422, 166 (1921). (8) Curtius, (9) Mettler, *Ber.* 37, 3693 (1904). (10) Sah, 443-449 (1936); *Cent.* 1936, II 2130; *C.A.* 30, 8148 (1936).

(11) Blakey, McCombie, Scarborough, *J. Chem. Soc.* 1926, 2867.

3:6775  $\gamma$ -CHLORO- $\beta$ -HYDROXY-*n*-PROPYL ACETATE  $C_5H_9O_3Cl$  Beil. II - 142  
(Glycerol  $\alpha$ -chlorohydrin  $\Pi_1$ - (67)  
 $\alpha'$ -acetate;  $\gamma$ -aceto- $\alpha$ -chlorohydrin;  $\Pi_2$ —  
 $\gamma$ -chloropropylene glycol  $\alpha$ -acetate)

$$\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}_2\text{O.CO.CH}_3 \end{array}$$

B.P. 240° (1) (2) at 760 mm. (3)

120-121° at 14 mm. (4)

[See also glycerol  $\alpha$ -chlorohydrin  $\beta$ -acetate (3:6517).]

[For prepn. of  $\bar{C}$  from epichlorohydrin (3:5358) with AcOH in a.t. at 180° for 24 hrs. (1) (2) or in pres. of anhydr.  $\text{FeCl}_3$  at room temp. (4) cf. (5); note, however, that the isomeric glycerol  $\alpha$ -chlorohydrin  $\beta$ -acetate (3:6517) is also formed.]

Note that the homogeneity of all reported preps. of  $\bar{C}$  is probably open to serious question.

3:6775 (1) Reboul, *Ann. Suppl.* 1, 232 (1861). (2) Bigot, *Ann. chim.* (6) 22, 491 (1891). (3) Gibson, *J. Soc. Chem. Ind.* 50, 950 (1931). (4) Knoevenagel, *Ann.* 402, 136-138 (1914). (5) Delaby, Dubois, *Bull. soc. chim.* (4) 47, 573 (1930).

3:6780  $\beta$ -HYDROXYETHYL CHLOROACETATE  $C_4H_7O_3Cl$  Beil. S.N. 160  
(Ethylene glycol mono-(chloroacetate))

$$\begin{array}{c} \text{CH}_2 \text{ CO.O.CH}_2\text{CH}_2 \\ | \qquad | \\ \text{Cl} \qquad \text{OH} \end{array}$$

B.P.  
240° dec. at 760 mm. (1)  $D_4^{20} = 1.330$  (2)  $n_D^{25} = 1.4585$  (1)  
86° at 1.6 mm. (2) 1.324 (2)  
85° at 0.15 mm. (1)  $n_D^{20} = 1.46090$  (2)  
84° at 0.95 mm. (2) 1.46049 (2)  
83° at 0.03 mm. (1)

Colorless odorless liq. — Miscible with aq. [diff. from ethylene glycol bis-(chloroacetate) (3:0720)].

[For prepn. of  $\bar{C}$  from ethylene oxide (1:6105) with chloroacetic acid (3:1370) in dry ether at 0° for 4 days (1) or at 50° for 6 days (2) see indic. refs.; from mono-sodium deriv. of ethylene glycol (1:6165) (1) or from ethylene glycol directly with chloroacetyl chloride (3:5235) in dry ether (1) or dioxane (2) see indic. refs.]

$\bar{C}$  on stdg. in ord. glass gradually disproportionates into ethylene glycol (1:6105) and

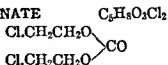
ethylene glycol *bis*-(chloroacetate) (3:0720) (1); this disproportionation may also occur during reactions of  $\bar{C}$  and thus lead to numerous by-prods. (see below).

[ $\bar{C}$  with diazomethane gives (19% yield (1))  $\beta$ -methoxyethyl chloroacetate (3:9285) accompanied by methyl chloroacetate (3:5585) and ethylene glycol *bis*-(chloroacetate) (3:0720).]

$\bar{C}$  on long stdg. with aq. is slowly hydrolyzed into ethylene glycol (1:6465) and chloroacetic acid (3:1370) (2).

3:6780 (1) Allen, Hibbert, *J. Am. Chem. Soc.* 56, 1398-1399 (1934). (2) Meerwein, Sönke, *J. prakt. Chem.* (2) 137, 316-319 (1933).

**3:6790 DI-( $\beta$ -CHLOROETHYL) CARBONATE**  
( $\beta,\beta'$ -Dichloroethyl  
carbonate).



Beil. III —  
III<sub>1</sub> —  
III<sub>2</sub>-(5)

B.P.

240-241° (1)  
115° at 8 mm. (1)

M.P.

+8.5° (1)

$D_4^{20} = 1.3506$  (1)

$n_D^{20} = 1.4610$  (1)

Colorless odorless liq. — Insol. in boil. aq. and not decomposed thereby. — Volatile with steam (1). — Requires solid  $\text{CO}_2$  + ether for solidification.

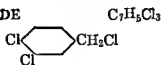
[For prepn. from  $\beta$ -chloroethyl chloroformate (3:5780) + ethylene chlorohydrin (3:5552) (70% yield) see (1).]

Hydrolyzes, but very slowly, even with warm alk. (1).

[For use as industrial solvent see (2) (3).]

3:6790 (1) Nekrassow, Komissarow, *J. prakt. Chem.* (2) 123, 164 (1929). (2) I.G., French 785,705, Aug. 17, 1935; *Cent.* 1936, I 1134. (3) I.G., Brit. 257,258, Aug. 11, 1926; *Cent.* 1927, I 820.

**3:6795 3,4-DICHLOROBENZYL CHLORIDE**



$\text{C}_7\text{H}_5\text{Cl}_3$

Beil. V - 300

V<sub>1</sub> —

V<sub>2</sub> —

B.P. 241° (1)

[For prepn. of  $\bar{C}$  from 3,4-dichlorotoluene (3:6355) at b.p. or from benzyl chloride (3:8535) in pres. of  $\text{I}_2$  on treatment with  $\text{Cl}_2$  see (1).]

$\bar{C}$  on oxidn. with  $\text{CrO}_3$  yields (2) 3,4-dichlorobenzoic acid (3:4925) q.v.

3:6795 (1) Beilstein, Kuhlberg, *Ann.* 146, 326-327 (1868). (2) Beilstein, Kuhlberg, *Ann.* 152, 224-226 (1869).

**— 2,6-DICHLORO-3-METHYLPHENOL**



$\text{C}_7\text{H}_5\text{OCl}_2$

Beil. VI —

VI<sub>1</sub> —

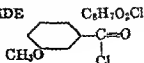
VI<sub>2</sub>-(356)

B.P. 241°

M.P. 27°

See 3:0150. Division A: Solids.

**3:6797 3-METHOXYBENZOYL CHLORIDE**  
(*m*-Anisoyl chloride)



Beil. X - 140

 $\Sigma_1$ —

B.P. 242.7–244.1°	at 760 mm. (1)
242–243°	at 733 mm. (2) (3)
148°	at 24 mm. (4)
122–123°	at 16 mm. (5)
123–125°	at 15 mm. (6)
123°	at 11 mm. (1)
110.8–111.0°	at 8.5 mm. (7)
81.5–82.0°	at 1 mm. (8)

[For prepn. of  $\bar{C}$  from *m*-methoxybenzoic acid (1:0703) with  $\text{PCl}_5$  (2) or with  $\text{SOCl}_2$  (yields: 92% (6), 86% (4), 78% (5)) (1) (7) see indic. refs.]

[Although 2-methoxybenzoyl chloride (3:6870) with anhydrous  $\text{Na}_2\text{CO}_3$  + pyridine gives the corresp. anhydride, this reactn. is not specifically recorded for  $\bar{C}$ ; however, 3-methoxybenzoic acid anhydride, cryst. from pet. eth., m.p. 66.6° (9), has been reported from 3-methoxybenzoic acid (1:0703) with  $\text{P}_2\text{O}_5$  (9).]

[ $\bar{C}$  with  $\text{C}_6\text{H}_6$  +  $\text{AlCl}_3$  (2) (said to be unsatisfactory because of autocondensation of  $\bar{C}$  to anthracene derivs. (3)) or better with  $\text{C}_6\text{H}_5\text{ZnBr}$  (62% yield (6)) yields 3-methoxybenzophenone (1:5141), m.p. 37° (6) (2), b.p. 342–343° at 730 mm. (2), 192° at 14 mm. (6). —  $\bar{C}$  with anisole (1:7445) +  $\text{AlCl}_3$  in  $\text{CS}_2$  (3) or in tetrachloroethane (5) gives (yields: 100% (5), 35% (3)) 3,4-dimethoxybenzophenone, pr. from alc., m.p. 58–59° (5), 55° (3).]

[ $\bar{C}$  with ethyl sodioacetacetate gives (61% yield (4) (10) ethyl *m*-methoxybenzoylacetoacetate;  $\bar{C}$  with methyl sodio- $\alpha$ -ethylacetoacetate gives (10) methyl  $\alpha$ -ethyl- $\alpha$ -(*m*-methoxybenzoyl)acetoacetate;  $\bar{C}$  with ethyl sodio- $\alpha,\gamma$ -dimethoxyacetoacetate gives (11) ethyl  $\alpha,\gamma$ -dimethoxy- $\alpha$ -(*m*-methoxybenzoyl)acetoacetate (for ketonic cleavage of these subst. acetoacetates see indic. refs.).]

[For reactn. of  $\bar{C}$  with 1,4-diaminoanthraquinone in prepn. of vat dyes see (12) (13).]

[ $\bar{C}$  with MeOH yields methyl *m*-methoxybenzoate (1:4111), b.p. 252°;  $\bar{C}$  with EtOH yields ethyl *m*-methoxybenzoate (1:4131), b.p. 260° (for study of rate of reactn. of  $\bar{C}$  with EtOH at 0° see (14) (8)).]

$\bar{C}$  on hydrolysis yields *m*-methoxybenzoic acid (1:0703), m.p. 109–110°.

3:6797 (1) Kabovec, Kohlrausch, *Z. physik. Chem. B* 38, 136 (1938). (2) Ullmann, Goldberg, *Ber.* 35, 2813–2814 (1902). (3) Lea, Robinson, *J. Chem. Soc.* 1926, 2354–2355 (4) Robinson, Rose, *J. Chem. Soc.* 1933, 1472. (5) Blicke, Weinkauff, *J. Am. Chem. Soc.* 54, 1449 (1932). (6) Martynoff, *Ann. chim.* (11) 7, 437–438 (1937). (7) Thompson, Norris, *J. Am. Chem. Soc.* 58, 1956 (1936). (8) Norris, Young, *J. Am. Chem. Soc.* 57, 1424 (1936). (9) Rule, Patterson, *J. Chem. Soc.* 125, 2161–2162. (10) Furukawa, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* 24, 320–324 (1934); *Cent.* 1935, I 1071.

(11) Pratt, Robinson, *J. Chem. Soc.* 127, 1185 (1925). (12) I.G., Swiss 136,249, Jan. 16, 1930, *Cent.* 1930, II 3462. (13) B.A.S.F., French 604,347, May 3, 1926; *Cent.* 1926, II 2358. (14) Norris, Fasce, Staud, *J. Am. Chem. Soc.* 57, 1415–1420 (1935).

— ***p*-XYLYLENE DICHLORIDE**

 $\text{C}_8\text{H}_8\text{Cl}_2$ 

Beil. V - 384

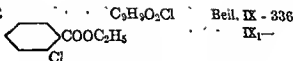
 $V_1$ -(186) $V_2$ -(300)

B.P. 240–245° dec.

M.P. 100°

See 3:2825. Division A: Solids.

## 3:6800 ETHYL o-CHLOROBENZOATE



B.P. 242.8-244.0°	(1)	$D_4^{15.4} = 1.1042$ (9)	$n_D^{15.4} = 1.52170$ (9)
243°	(2) (3)		
242°	(4)		
238-242°	(5)		
130°	at 20 mm. (6)		
124.8-125.1°	at 20 mm. (1)		
122.5°	at 15 mm. (7) (8)		

[For prepn. of  $\bar{C}$  from *o*-chlorobenzoic acid (3:4150) with EtOH + HCl see (2); from *o*-chlorobenzoyl chloride (3:6640) with abs. EtOH see (5) (1).]

[C on electrolytic reductn. in alc./H<sub>2</sub>SO<sub>4</sub> soln. yields (10) mainly *o*-chlorobenzyl ethyl ether [Beil. VI-444; VI<sub>1</sub>-(222)], b.p. 212° (10), together with a little *o*-chlorobenzyl alc. [Beil. VI-444; VI<sub>1</sub>-(222)], ndls. from dil. alc., m.p. 72° (10).]

[C̄ with C<sub>6</sub>H<sub>5</sub>MgBr in ether as directed (11) yields α,α'-bis-(o-chlorophenyl)-α,α'-diphenyl-ethylene glycol (*sym*-2,2'-dichlorobenzpinacol) [Beil. VI- (523)].]

○ in alc. on refluxing with hydrazine hydrate yields (14) (15) *o*-chlorobenzhydrazide, white ndls. from alc., m.p. 117–118° (15), 109–110° (14). [This prod. with BzH yields benzal-*o*-chlorobenzhydrazide, white ndls. from 95% alc., m.p. 162° (15).] [For use of *o*-chlorobenzhydrazide as react. for identification of aldehydes and ketones see (15).]

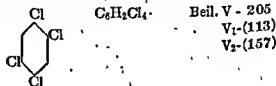
$\bar{C}$  on hydrolysis (Sap. Eq. = 184.5) yields ethyl alcohol (1:6130) + *o*-chlorobenzoic acid (3:4150). [For studies of hydrolysis of  $\bar{C}$  under various conditions see (7) (8) (12) (13) (3) (6).] — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see *o*-chlorobenzoic acid (3:4150).

3: 6800 (1) Kohlrausch, Stockmair, *Monatsh.* 66, 324 (1935). (2) Glutz, *Ann.* 143, 196 (1867).  
(3) Kindler, *Ann.* 464, 287 (1928). (4) Vavon, Barbier, Thiebaut, *Bull. soc. chim.* (5) 1, 813  
(1934). (5) Kekulé, *Ann.* 117, 153-154 (1861). (6) Evans, Gordon, Watson, *J. Chem. Soc.*  
1937, 1420-1422. (7) McColl, *Can. J. Chem.* 1, 177 (1915). (8) Cashmore,  
*ibid.*, *Ann.* 422, 166 (1921).

Settle, *J. Chem. Soc.* 121, 1926, 2867. (14) Kalb,

Gross, Ber. 59, 732 (1926). {15} Sun, Sah, *Science Repts. Natl. Tsing Hua Univ.* A-2, 359-363 (1934); *Cent.* 1935, I 57; *C.A.* 29, 466 (1935).

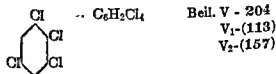
— 1,2,4,5-TETRACHLOROBENZENE



B.P. 243-246° cor. M.P. 141°

See 3:4115. *Division A: Solids.*

## 1,2,3,5-TETRACHLOROBENZENE



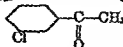
B.P. 246° cor. M.P. 51°

See 3:0915. *Division A: Solids.*

3:6815 *m*-CHLOROACETOPHENONE  
(*m*-Chlorophenyl  
methyl ketone)

 $C_8H_7OCl$ 

Beil. S.N. 639



B.P. 241-245° at 744 mm. (1)

 $D_4^{20} = 1.2130$  (2)

227-229° (2)

127-131° at 30 mm. (3)

113° at 11 mm. (4)

Colorless liq. with aromatic odor. — Volatile with steam.

[For prepn. of  $\bar{C}$  from *m*-chlorophenyl-phenyl-carbinol (2) by oxidn. with  $CrO_3/AcOH$  (90% yield) see (2); from *m*-aminosacetophenone [Beil. XIV-45, XIV-1-(365)] via diazotization and use of  $Cu_2Cl_2$  reactn. (45% yield (4)) see (4) (3); from methyl *m*-chlorobenzoyl-acetate (2) by hydrolysis with 20%  $H_2SO_4$  for 12 hrs. (65% yield) see (2).]

[For study of rate of reactn. with  $Br_2$  see (4).] $\bar{C}$  on htg. with 50% KOH as directed (1) gives 14% yield *m*-chlorobenzoic acid (3:4392).④ *m*-Chloroacetophenone oxime: cryst. from AcOH, m.p. 88° (2) (1).④ *m*-Chloroacetophenone *p*-nitrophenylhydrazone: maroon cryst. from AcOH, m.p. 175-176° (2). (The phenylhydrazone of  $\bar{C}$  is unstable (2).)④ *m*-Chloroacetophenone semicarbazone: cryst. from alc., m.p. 232° (3).

3:6815 (1) Lock, Böck, *Ber.* 70, 920-921 (1937). (2) Wahl, Rolland, *Ann. chim.* (10) 10, 29-30 (1928). (3) Edkins, Linnell, *Quart. J. Pharm. Pharmacol.* 9 75-109; *Cent.* 1937, I 4780; *C.A.* 30, 6349 (1936). (4) Evans, Morgan, Watson, *J. Chem. Soc.* 1935, 1172.

3:6825 *p*-CHLOROBENZOTRICHLORIDE $C_7H_4Cl_4$ 

Beil. V - 303


 $V_1$ —  
 $V_2$ —

B.P. 245° (1)

99-100° at 4.9 mm. (2)

[For prepn. of  $\bar{C}$  from *p*-hydroxybenzoic acid (1:6840) (3) (or the "*p*-hydroxybenzid" [Beil. X-154] obtd. from it by htg. (4)) with  $PCl_5$  see indic. refs.; from *p*-toluenesulfonyl chloride [Beil. XI-103, XI-1-(26)] with  $Cl_2$  at 150-200° see (5); from *p*-chlorotoluene (3:8287) with  $Cl_2$  at high temp. in u.v. light see (2); for formn. of  $\bar{C}$  (together with other products) from benzotrichloride (3:6540) with  $Cl_2$  under various circumstances see (1) (6) (7); for purification of  $\bar{C}$  see (8).]

[For use of  $\bar{C}$  with NaOAc in prepn. of acetic anhydride see (9); for use of  $\bar{C}$  htd. with *p*-chlorobenzoic acid (3:4940) +  $ZnCl_2$  +  $FeCl_3$  in prepn. of *p*-chlorobenzoyl chloride (3:6550) see (10); for use of  $\bar{C}$  with dichloroacetic acid (3:6208) +  $H_2SO_4$  in prepn. of a mixt. of *p*-chlorobenzoyl chloride (3:6550) and dichloroacetyl chloride (3:5290) see (11).]

[For condens. of  $\bar{C}$  with 1-hydroxynaphthoic acid-2 [Beil. X-331, X-1-(144)] in prepn. of dyestuff intermediates see (12); for react. of  $\bar{C}$  with  $\alpha$ -naphthol (1:1500) to yield 1-hydroxy-4-(*p*-chlorobenzoyl)naphthalene see (13).]

[ $\bar{C}$  htd. with 99% HF (14) (15) or with  $2SbF_5 \cdot NH_4HF_2$  at 150-160° (16) gives (86% yield (14)) *p*-chlorobenzotrifluoride, b.p. 137-138° (15).]

$\bar{C}$  on hydrolysis, e.g., by htg. with aq. in a.t. at 200° (1), yields *p*-chlorobenzoic acid (3:4940) q.v.

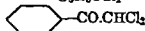
3:6825 (1) Beilstein, Kuhlberg, *Ann.* 150, 295-296 (1869). (2) Maryott, Hobbs, Gross, *J. Am. Chem. Soc.* 62, 2321 (1940). (3) Anschütz, Moore, *Ann.* 239, 346-348 (1887). (4) Klepf,

*J. prakt. Chem.* (2) 28, 204-205 (1853). (5) Gilliard, Monnet, Cartier, *Ger.* 98,433, Dec. 12, 1896; *Cent.* 1898, II 800. (6) Spreckels, *Ber.* 52, 319 (1919). (7) Wertyporoch, *Ann.* 493, 157-161 (1932). (8) Britton (to Dow Chem. Co.), U.S. 1,804,458, May 12, 1931; *Cent.* 1931, II 497; *C.A.* 25, 3668 (1931). (9) Dr. A. Wacker Ges. für Elektrochem. Ind., Kaufler, Hormann, *Brit.* 165,747, June 30, 1921; *Cent.* 1922, II 1218. (10) Scottish Dyes, Ltd., Bangham, Thomas, *Brit.* 308,231, April 18, 1929; *Cent.* 1929, II 1348.

(11) Mills (to Dow Chem. Co.), U.S. 1,965,556, July 3, 1934; *Cent.* 1934, II 2899; *C.A.* 28, 5174 (1934). (12) Soc. Chem. Ind. Basel, *Ger.* 335,115, June 21, 1922; Swiss 92,406, Feb. 16, 1923; *Cent.* 1923, II 484. (13) Soc. Chem. Ind. Basel, *Ger.* 418,033, Aug. 26, 1925; *Cent.* 1925, II 2095. (14) Osswald, Müller, Steinhauser (to I.G.), *Ger.* 575,593, May 22, 1933; *Cent.* 1933, II 609. (15) I.G., French 745,293, May 8, 1933; *Cent.* 1933, II 2061. (16) I.G., French 809,301, March 1, 1937; *Cent.* 1937, I 4863; *C.A.* 31, 6675 (1937).

3:6835  $\omega,\omega$ -DICHLOROACETOPHENONE $C_8H_6OCl_2$ 

Beil. VII - 282

VII<sub>1</sub>-(152)

B.P.		M.P.	
245°	at 760 mm. (1)	20-21.5°	(7)
247-248°	dec. (2)	19°	(2)
249°	(3)	Not frozen at -10°	(1)
143°	at 25 mm. (2)		
142-144°	at 25 mm. (11)		
138-140°	at 13 mm. (5)		
132-134°	at 13 mm. (11)		
131-132°	at 11 mm. (6)		
128-129°	at 14 mm. (4)		
121-122°	at 10 mm. (1)		

## Lachrymatory oil.

[For prepn. from acetophenone (1:5515) by actn. of  $Cl_2$  (100% yield (4) (5)) in AcOH (80-94% yield (11)) see (4) (2) (11) or of suluryl chloride see (1); from phenylacetylene (1:7425) by actn. of  $HOCl$  (7),  $CH_3OCl$  (6), or  $C_2H_5OCl$  (5) see (7) (6) (5); from  $C_6H_6$  + dichloroacetyl chloride (3:5290) (2) or dichloroacetonitrile (4) +  $AlCl_3$  see (2) (4).]

$\bar{C}$  is almost unchanged by boiling with aq. (2). —  $\bar{C}$  on shaking with 20 pts. 2 N aq. NaOH dissolves in 1-2 min.; after boiling under reflux for a few min. and acidifying, extraction with ether gives in 95% yield (5) 85-90% yield (11) *d,l*-mandelic ac. (1:0465), cryst. from  $CHCl_3$  + pet. eth., m.p. 118.5° (8).

$\bar{C}$  on oxidn. with alk.  $KMnO_4$  yields (1) (2) (3) (5) (5) benzoic ac. (1:0715), m.p. 121°. [ $\bar{C}$  on treatment with NaOH + NaOCl in the cold yields benzoic ac. (1:0715) and chloroform in proportions depending upon conditions (9).] [Note that *d,l*-mandelic ac. (see above) may also be formed owing to actn. of alk. upon  $\bar{C}$  cf. (9).]

$\bar{C}$  on nitration yields *m*-nitro- $\omega,\omega$ -dichloroacetophenone, m.p. 57-58° (10).

$\bar{C}$  in alc. treated with excess alk.  $NH_2OH$  for 7-10 hrs. yields (6) phenylglyoxaldioxime [Beil. VII-672], cryst. from  $CHCl_3$ , m.p. 168° (5). [The product, m.p. 150-152°, so obtd. by (5) may have been a mixt. of the high-melting stereoisomer, m.p. 180°, with the low-melting stereoisomer, m.p. 168°.]

3:6835 (1) Durrans, *J. Chem. Soc.* 121, 46 (1922). (2) Gautier, *Ann. chim.* (6) 14, 345-347, 385-387 (1888). (3) Béhal, *Bull. soc. chim.* (2) 50, 634 (1888). (4) Houben, Fischer, *Ber.* 64, 2647-2648 (1931). (5) Goldschmidt, Endres, Dirsch, *Ber.* 58, 575-576 (1925). (6) Jackson, *J. Am. Chem. Soc.* 56, 977-978 (1934). (7) Wittorf, *J. Russ. Phys.-Chem. Soc.* 32, 88-117 (1900); *Cent.* 1900, II 30. (8) Houben, Fischer, *Ber.* 64, 2644-2645 (1931). (9) Aston, Newkirk, Dorsky, Jenkins, *J. Am. Chem. Soc.* 64, 1413-1416 (1942). (10) Raŋiewicz-Zubkowski, *Roczniki Chem.* 9, 532-537 (1929); *C.A.* 24, 92 (1930).

(11) Aston, Newkirk, Jenkins, Dorsky, *Org. Syntheses* 23, 48-51 (1943).

3:6840	3-CHLOROPROPANEDIOL-1,2 DIACETATE	$C_7H_{11}O_4Cl$	Beil. II - 142
	( $\gamma$ -Chloropropylene glycol diacetate, glycerol $\alpha$ -monochlorohydrin diacetate, " $\alpha$ -monochlorohydrin" diacetate)	$  \begin{array}{c}  CH_2Cl \\    \\  HC-OOCCH_3 \\    \\  CH_2OOCCH_3  \end{array}  $	$\Pi_1$ -(67) $\Pi_2$ -

B.P.				
245°	at 740 mm.	(1)	$D_4^{25} = 1.199$ (5)	$n_D^{25} = 1.4386$ (5)
145-150°	at 40 mm.	(2)		
142-149°	at 40 mm.	(3)		$n_D^{20} = 1.4407$ (8)
116°	at 12 mm.	(4)		
116-118°	at 11 mm.	(10)		
115-117°	at 10 mm.	(5)		
113-114°	at 9 mm.	(6)		
102-105°	at 6 mm.	(7)		
96.5-97°	at 0.4-0.6 mm.	(7)		
90-91°	at 0.8 mm.	(8)		

[For prepn. of  $\bar{C}$  from glycerol  $\alpha$ -monochlorohydrin (3:9038) with  $Ac_2O$  (1:1015) (75% yield (6)) cf. (9) in pres. of a trace of  $H_2SO_4$  (100% yield (4)) see indic. refs.; from epichlorohydrin (3:5358) with  $Ac_2O$  (1:1015) at 180° (1) (5) or in pres. of anhydrous  $FeCl_3$  at ord. temp. (10) see indic. refs.; from 3-hydroxy-1,2-epoxypropene (glycidol) with large excess  $AcCl$  (3:7065) on htg. as directed (69% yield (7)) or from glyceryl-glycidol with  $AcCl$  (3:7065) at 60° for 2 hrs. (37% yield (8)) see indic. refs.]

[For prepn. of  $\bar{C}$  from glycerol (1:6540) with  $AcOH + HCl$  see (11); from glyceryl  $\alpha, \alpha'$ -diacetate with  $Ac_2O + HCl$  see (3); from glyceryl triacetate (triacetin) in dry ether at 0° with  $HCl$  gas (2) (3) cf. (4) see indic. refs.]

[ $\bar{C}$  in  $MeOH$  contg. 1%  $HCl$  at 60° for 6 hrs. gives (80% yield (8)) 3-chloropropanediol-1,2 (glycerol  $\alpha$ -monochlorohydrin) (3:9038).]

3:6840 (1) Truchot, *Compt. rend.* 61, 1170 (1865); *Ann.* 138, 299 (1866). (2) de la Acena, *Compt. rend.* 139, 808 (1904). (3) Seelig, *Ber.* 24, 3469-3471 (1891). (4) Wegscheider, *Zmesnikar, Monatsk.* 34, 1068-1071 (1913). (5) Gibson, *J. Soc. Chem. Ind.* 50, 949-954 (1931). (6) Nivière, *Compt. rend.* 156, 1777 (1913); *Bull. soc. chim.* (4) 15, 82-83 (1914). (7) Ruder, *J. Am. Chem. Soc.* 54, 775 (1932). (8) Sjöberg, *Svensk Kem. Tid.* 63, 454-457 (1941); *Cent.* 1942, II 25; *C.A.* 37, 4363 (1943). (9) Abderhalden, Eichwald, *Ber.* 47, 1859 (1914). (10) Knoevenagel, *Ann.* 402, 135-138 (1914).

(11) Berthelot, de Luca, *Ann. chim.* (3) 52, 451 (1858).]

# 3,4,5-TRICHLOROTOLUENE



$C_7H_5Cl_3$	Beil. V - 299
	$V_1$ —
	$V_2$ —

B.P. 245.5-247° at 768 mm. M.P. 44.5-45.5°

See 3 0580. Division A: Solids.



## — 2,4,6-TRICHLOROPHENOL



Beil. VI—

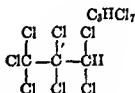
VI<sub>1</sub>—VI<sub>2</sub>-(180)

B.P. 244-248° at 746 mm.

M.P. 67-68°

See 3:1620. Division A: Solids.

## — 1,1,1,2,2,3,3-HEPTACHLOROPROPANE



Beil. I - 108

I<sub>1</sub>-(35)I<sub>2</sub>-(73)

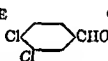
B.P. 247-248° sl. dec.

M.P. 20-30°

 $D_4^{25} = 1.8043$ 

See 3:0200. Division A: Solids.

## — 3,4-DICHLOROBENZALDEHYDE



Beil. VII - 238

VII<sub>1</sub>-(134)

B.P. 247-248°

M.P. 43-44°

See 3:0550. Division A: Solids.

3:6845 *m*-CHLOROBENZOTRICHLORIDE

Beil. V - 303

V<sub>1</sub>—V<sub>2</sub>—

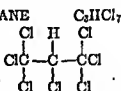
B.P. 247-250° (1)

[For prepn. from *m*-hydroxybenzoic acid (1:0825) (1) or from *m*-sulfobenzoic acid [Beil. XI-384, XI<sub>1</sub>-(98)] (2) with  $PCl_5$  see indic. rels.; for studies on formn. of  $\bar{C}$  from benzotrichloride (3:6540) with  $Cl_2$  see (3) (4); for purification of  $\bar{C}$  see (5).]

[For condens. of  $\bar{C}$  with 1-hydroxynaphthoic acid-2 [Beil. X-331, XI<sub>1</sub>-(144)] in prepn. of dyestuff intermediates see (6).]

$\bar{C}$  on hydrolysis presumably yields *m*-chlorobenzoic acid (3:4302) q.v.

3:6845 (1) Anschütz, Moore, *Ann.* 239, 342 (1887). (2) Kämmerer, Carius, *Ann.* 131, 158 (1864). (3) Spreckels, *Ber.* 52, 310 (1919). (4) 31; *Cent.* 1931, II 497; *C.A.* 25, 3668 (1922; Swiss, 92,408, Feb. 16, 1923; *Cent.* 1923, II 484).

3:6860 1,1,1,2,3,3,3-HEPTACHLOROPROPANE  
(sym.-Heptachloropropane)

Beil. I —

I<sub>1</sub>-(35)I<sub>2</sub>—

B.P.

240°

(1)

105°

at 90 mm. (1)

105-132° at 20 mm. (2)

M.P.

11-11.5° (1)

 $D_4^{25} = 1.7921$  (1) $n_D^{25} = 1.5427$  (1)

Oil with disagreeable odor.

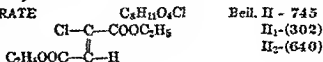
[For prepn. from trichloroethylene (3:5170) +  $\text{CCl}_4$  +  $\text{AlCl}_3$  (49% yield (2)) by stdg. 48 hrs. at 20–30° (2) see (2) (1).]

$\bar{\text{C}}$  dislvd. in  $\text{CCl}_4$  and heated at 60–70° with  $\text{AlCl}_3$  evolves  $\text{HCl}$  and gives (83% yield (3)) hexachloropropene (3:6370).

$\bar{\text{C}}$  in alc. on titration with alk. gives (3) an apparent Neut. Eq. of 285.5 by loss of 1  $\text{HCl}$  and formation of hexachloropropene (3:6370).

3:6860 (1) Prins, *J. prakt. Chem.* (2) 89, 417 (1914). (2) Henne, Ladd, *J. Am. Chem. Soc.* 60, 2494–2495 (1938). (3) Prins, *Rec. trav. chim.* 54, 251 (1935).

### 3:6864 DIETHYL CHLOROFUMARATE



B.P.

250°	at 760 mm., sl. dec.	(1)	$D_4^{24} = 1.19517$ (7)	$n_D^{24} = 1.4598$ (7)
243–245° u.c.	at 735 mm.	(10)		
202–203°	at 210 mm.	(1)	$D_4^{20} = 1.188$ (8)	$n_D^{20} = 1.4571$ (8)
136.5° cor.	at 19 mm.	(2)	1.187 (8)	1.4561 (8)
135–136°	at 17 mm.	(8)	1.183 (4)	
127°	at 10 mm.	(3)		
119°	at 12 mm.	(4)	$D_4^{18.3} = 1.1890$ (8)	$n_D^{18.3} = 1.45782$ (8)
117°	at 7 mm.	(5)		
108°	at 16 mm.	(6)	$D_4^{18.2} = 1.1903$ (8)	$n_D^{18.2} = 1.45723$ (8)
			$D_4^{16.3} = 1.1822$ (4)	$n_D^{16.3} = 1.45979$ (4)

[See also diethyl chloromaleate (3:6697).]

Colorless liq. with irritating actn. on skin and whose vapor strongly attacks the eyes. — Insol. cold aq., eas. sol. alc., ether; volatile with steam.

[For prepn. of  $\bar{\text{C}}$  from chlorofumaric acid (3:4853) in abs. EtOH with  $\text{HCl}$  gas (1) or conc.  $\text{H}_2\text{SO}_4$  (4) see indic. refs.; from chlorofumaryl (di)chloride (3:6105) with EtOH see (10) (1) (9) (3).]

[For formn. of  $\bar{\text{C}}$  from diethyl *d*-tartrate (1:4256) with  $\text{PCl}_5$  see (11) (note that ethyl hydrogen chlorofumarate, cryst. from pet. ether, m.p. 52–53°, has also been obt'd. (12) as one of the prods. of this reactn.); from diethyl *d,l*-(7)- $\alpha,\alpha$ -dichlorosuccinate by loss of  $\text{HCl}$  under actn. of dimethylaniline see (5).]

[ $\bar{\text{C}}$  (1 mole) with diethyl sodio-malonate (1 mole) is said (13) to yield tetraethyl cyclopropane-1,1,2,3-tetracarboxylate [Beil. IX-991] although no details are given; in the presence of excess  $\text{NaOEt}$  in cold alc. for 12 hrs., however, the same components give (15–20% yield (14)) (15) triethyl  $\gamma$ -carbethoxyaconitate [Beil. II-876], b.p. 205–207° at 16 mm. (14); for reactn. of  $\bar{\text{C}}$  (1 mole) with diethyl mono- and di-substituted malonates yielding triethyl corresp. subst. aconitates see (13) —  $\bar{\text{C}}$  (1 mole) with ethyl sodioacetate (1 mole) in abs. alc. refluxed for  $\frac{1}{2}$  hr. gives (72% yield (3)) (16) triethyl  $\gamma$ -acetyl-aconitate [Beil. III-860], yel. oil, b.p. 187–188° at 15 mm. (3), the same as similarly obt'd. (3) from diethyl chloromaleate (3:6697).]

[ $\bar{\text{C}}$  with *o*-chlorophenol (3:5950) or its Na deriv. in boilg. xylene for 2 hrs. gives (77% yield (17)) diethyl *o*-chlorophenoxyfumarate, b.p. 203–204° at 14 mm. (17). —  $\bar{\text{C}}$  with *p*-chlorophenol (3:0475) +  $\text{NaOEt}$  gives (17) diethyl *p*-chlorophenoxyfumarate, b.p. 199–200° at 12 mm. (17).]

The reactn. of  $\bar{C}$  with  $NH_3$  under various circumstances is disputed and confused and cannot profitably be discussed here; for refs. see Beil. II-745.

$\bar{C}$  (1 mole) with hydrazine hydrate (2 moles) directly (18) or in alc. or AcOH (9) yields ethyl pyrazolone-5 (or 3)-carboxylate-3 (or 5) [Beil. XXV-206, XXV-1-(567)], ndls. from boilg. aq., m.p. 184-185° (18); 178° (9); note that in the direct treatment with just 2 moles of hydrazine hydrate much heat is evolved and the product ppts. on cooling; if excess base is employed (in which the prod. is soluble) neutralization with acid is necessary.

[ $\bar{C}$  with phenylhydrazine reacts much more slowly; however, after several hrs. at 100° phenylhydrazine HCl ppts. leaving an oil from which a cryst. prod. spar. sol. in boilg. AcOH hut sepg. from it in colorless ndls., m.p. 272° dec., can be obt'd. (18); this prod. is not, however, the ethyl 1-phenylpyrazolone-5(or 3)-carboxylate-3(or 5) which might be expected, hut is regarded [Beil. XXVI-578] (18) as a 4,4'-bis derivative of it.

$\bar{C}$  on boilg. with 1:1 HCl and subsequent evapn. to dryness undergoes hydrolysis yielding (4) chlorofumaric acid (3:4853), m.p. 191.5° (4).

3:6864 (1) Perkin, *J. Chem. Soc.* 53, 700-703 (1888). (2) Walden, Swinne, *Z. physik. Chem.* 79, 742 (1912). (3) Ruhemann, Tyler, *J. Chem. Soc.* 69, 532-535 (1896). (4) von Auwers, Harres, *Ber.* 62, 1679, 1085-1687 (1929). (5) Darzens, Sejourne, *Compt. rend.* 154, 1617 (1912). (6) von Auwers, Harres, *Z. physik. Chem.* A-143, 10 (1929). (7) Gladstone, *J. Chem. Soc.* 59, 293 (1891). (8) von Auwers, Schmidt, *Ber.* 46, 481 (1913). (9) Ruggli, Hartmann, *Helv. Chim. Acta* 3, 513 (1920). (10) Claus, *Ann.* 191, 80-93 (1878).

(11) Henry, *Ann.* 156, 178-179 (1870). (12) Patterson, Todd, *J. Chem. Soc.* 1929, 1765-1770. (13) Ruhemann, *J. Chem. Soc.* 81, 1212-1214 (1902). (14) Desai, *J. Chem. Soc.* 1932, 1089-1090. (15) Bland, Thorpe, *Proc. Chem. Soc.* 23, 131 (1912). (16) Ruhemann, *J. Chem. Soc.* 71, 323-324 (1897). (17) Ruhemann, *Ber.* 54, 916-918 (1921). (18) Ruhemann, *J. Chem. Soc.* 69, 1394-1397 (1896).

— 2,3,6-TRICHLOROPHENOL



Beil. VI - 190

VI<sub>1</sub>—

VI<sub>2</sub>-(180)

B.P. 252-253° u.c.

M.P. 58°

See 3:1160. Division A: Solids.

— 3,4-DICHLOROPHENOL



Beil. VI - 190

VI<sub>1</sub>-(103)

VI<sub>2</sub>-(179)

B.P. 253.5° at 757 mm.

M.P. 65°

See 3:1460. Division A: Solids.

— 1,2,3,4-TETRACHLOROBENZENE



Beil. V - 204

V<sub>1</sub>—

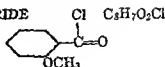
V<sub>2</sub>-(156)

B.P. 254° cor. at 761 mm.

M.P. 45-46°

See 3:0655. Division A: Solids.

## 3:6870 2-METHOXYBENZOYL CHLORIDE

(o-Anisoyl chloride;  
salicyloyl chloride methyl ether)Beil. X - 85  
X<sub>1</sub>-(43)

B.P. 254° u.c.	at 760 mm. (1)
133°	at 19 mm. (2)
145° cor.	at 17 mm. (3)
136°	at 12 mm. (4)
128°	at 11 mm. (5)
128.8-129.0°	at 8 mm. (6)
119.6°	at 1 mm. (7)
105-106°	at 1 mm. (8)

Colorless liquid.

[For prepn. of  $\bar{C}$  from o-methoxybenzoic acid (o-anisic acid) (1:0685) with  $PCl_5$  (1) (4) (9) (10) (11) (every trace of salicylic acid must first be removed (9)) or with  $SOCl_2$  (2) (3) (4) (5) (6) (7) (12) (prolonged heating tends to demethylate product (4)) see indic. refs.; note that for none of the preps. is the yield recorded.]

[ $\bar{C}$  on cat. reductn. at 250° with  $H_2$  at ord. press. in pres. of Pd gives (11), not the expected o-methoxybenzaldehyde, but instead o-methoxytoluene (methyl o-tolyl ether) (1:7480).]

$\bar{C}$  with anhydrous  $Na_2CO_3$  in pyridine shaken for  $\frac{1}{2}$  hr., poured onto ice, yields (13) o-methoxybenzoic acid anhydride, ndls. from pet. ether, m.p. 72.4° (13).

[ $\bar{C}$  with  $C_6H_6$  +  $AlCl_3$  gives (14) (9) (2) (12) o-hydroxybenzophenone (1:1414) (note demethylation of intermediate o-methoxybenzophenone (1:5142) and also the formn. in small amt. (12) of 2-hydroxy-5-(2'-hydroxybenzoyl)benzophenone, m.p. 131-132° (12)).]

[ $\bar{C}$  with  $Et_2Zn$  gives (87% yield (3)) ethyl 2-methoxyphenyl ketone [Beil. VIII-102], b.p. 137° cor. at 18 mm. (3).]

[For reaction of  $\bar{C}$  with ethyl sodio-acetoacetate (5), with ethyl sodio- $\alpha$ -methylacetoacetate (15), with ethyl sodio- $\alpha$ -allylacetoacetate (16), or with ethyl sodio- $\alpha,\gamma$ -dimethoxyacetoacetate (17) (together with hydrolytic cleavage of the resulting products to ketones and/or acids) see indic. refs.; for reactn. of  $\bar{C}$  with Na phenylacetylene and ring closure of intermediate to corresp. 2-methoxyflavone see (18).]

[ $\bar{C}$  (1 mole) with HCN (4 moles) in dry ether + pyridine gives (4) o-methoxybenzoyl cyanide, yel. ndls. from lgr., m.p. 56°, b.p. 161° at 12 mm. (4).]

[ $\bar{C}$  with urea refluxed in  $C_6H_6$  for 15 hrs. gives (19) N-(o-methoxybenzoyl)urea, ndls. from hot aq. or toluene, m.p. 192° (19).]

[ $\bar{C}$  with methyl salicylate gives (20) methyl O-(2-methoxybenzoyl)salicylate, m.p. 102-104° (20);  $\bar{C}$  with salicylamide in pyridine gives (21) N-(2-methoxybenzoyl)salicylamide, m.p. 189° (21).]

[ $\bar{C}$  with MeOH yields methyl o-methoxybenzoate (1:4091), b.p. 248°;  $\bar{C}$  with EtOH yields ethyl o-methoxybenzoate (1:4151), b.p. 261°; for study of rate of reactn. of  $\bar{C}$  with EtOH at 0° see (22) (8).]

$\bar{C}$  on hydrolysis yields o-methoxybenzoic acid (1:0685), m.p. 100-101°; for the amide, anilide, and other derivs. corresp. to  $\bar{C}$  see o-methoxybenzoic acid (1:0685).

- 3:6870 (1) Pinnow, Müller, Ber. 28, 158 (1895). (2) Staudinger, Kon. Ann. 384, 99 (1911).  
 (3) Fischer, Slimmer Ber. 28, 158 (1895). (4) March, Ber. 28, 158 (1895). (5) von A.  
 B-38, 136 (1938).  
 J. Am. Chem. Soc. 60, 177 (1938).  
 Cohen, Dudley, J. Am. Chem. Soc. 60, 177 (1938).

## 3:6878 1-CHLORONAPHTHALENE

 $C_{10}H_7Cl$ 
 Beil. V - 541  
 V<sub>1</sub>-(262)  
 V<sub>2</sub>-(444)

B.P.	F.P.		
[263°	(1)] -2.3° (9)	$D_4^{25} = 1.192$	(6)
[259-262°	(2)] -2.5° (5)		
259.4-260.3° at 760 mm.	(3) -4° (12)	$D_4^{21.6} = 1.1906$	(7)
259.3° at 760 mm.	(4) (5)		
258.8° at 753 mm.	(6)	$n_D^{21.6} = 1.63184$	(7)
258° cor.	(7)		
255.5-256.0°	(8)	$D_4^{20} = 1.19382$	(4)
255.6° cor. at 752 mm.	(9)	. 1.192	(7)
248.6° at 600 mm.	(4)		
230.8° at 400 mm.	(4)	$n_D^{20} = 1.63321$	(4) (7)
204.2° at 200 mm.	(4)		
180.4° at 100 mm.	(4)	$D_{15}^{15} = 1.1966$	(9)
171.4° at 75 mm.	(4)		
159.3° at 50 mm.	(4)		
144.0-146.5° at 29 mm.	(10)		
140.3° at 25 mm.	(4)		
129.54° at 16 mm.	(5)		
125.4° at 16 mm.	(11)		
127.97° at 15 mm.	(5)		
126.25° at 14 mm.	(5)		
122.0-122.2° at 13 mm.	(3)		
118.6° at 10 mm.	(4)		
104.8° at 5 mm.	(4)		
85.3° at 1.5 mm.	(4)		

Colorless oil, volatile with steam. — Note that presence of as much as 10% of 2-chloronaphthalene (3:1285) has no effect upon density of  $\bar{C}$  (9). — Note also that addn. of 1,4-dichloronaphthalene (3:1655), m.p. 68°, or of 1,6-dichloronaphthalene (3:0310), m.p. 48°, lowers m.p. of  $\bar{C}$  (9).

[For sepn. of mixts. of  $\bar{C}$  with the isomeric 2-chloronaphthalene by fractional freezing of their soln. in appropriate solvents see (6). — For purification of tech.  $\bar{C}$  by treatment with 1-2% alk. at 150° under reduced press. see (13). — For sepn. of  $\bar{C}$  from dichloronaphthalenes by means of its const.-boil. mixt. (b.p. 99°) with aq. see (18).]

[For prepn. of  $\bar{C}$  from  $\alpha$ -naphthylamine [Beil. XII-1212, XII<sub>1</sub>-(519)] via diazotization and use of  $Cu_2Cl_2$  reactn. (70-75% yield (9)) (8) (7) or even by warming diazo soln. with HCl (10-20% yield (14)) or from diazonium/ $ZnCl_2$  cpd. on addn. to phenol at 60° (46%  $\bar{C}$  + 29% hydroxybiphenyl + 20% diphenyl ether (52)) see indic. refs.; from  $\alpha$ -naphthalenesulfonyl chloride [Beil. XI-157, XI<sub>1</sub>-(37)] (2), or from 1-nitronaphthalene [Beil. V-553, V<sub>1</sub>-(264)] (15), or from  $\beta$ -naphthol (1:1500) (16) with  $PCl_5$  as directed see indic. refs.; for formn. of  $\bar{C}$  from 1-nitronaphthalene with  $Cl_2$  see (17).]

[For prepn. of  $\bar{C}$  from naphthalene with  $Cl_2$  in boilg. naphthalene (19) (48), in vapor phase (20) (22) (27), in various solvents (21) (22) (23) (24) (25) (26) see indic. refs.; from naphthalene with HCl gas + air in pres. of cat. see (28); from naphthalene with  $PbCl_4 \cdot 2NH_4Cl$  at 140-150° (29) or with  $SO_2Cl_2$  +  $AlCl_3$  (79% yield (30)) see indic. refs.; from

naphthalene dichloride [Beil. V-519] with boilg. alc. KOH (31) cf. (32) or by distn. (33) cf. (34) see indic. refs.]

[For thermal anal. of systems of  $\bar{C}$  with  $SbBr_3$  see (35); with  $PkOH$  see (36); with 2,4,6-trinitroresorcinol (styphnic acid) see (37).]

[ $\bar{C}$  with  $Cl_2$  io cold or  $\bar{C}$  with  $Cl_2$  io lt. pet. yields (38) 1-chloroonaphthalene tetrachloride, m.p. 131° (38), and 1,4-dichloroonaphthalene (3.1655), m.p. 68° (38);  $\bar{C}$  with  $Cl_2$  io  $CHCl_3$  yields (38) the above 1-chloroonaphthalene tetrachloride and 1,4-dichloroonaphthalene tetrachloride, m.p. 172° (38);  $\bar{C}$  with  $Cl_2$  io  $CS_2$  gives (38) a new dichloroonaphthalene tetrachloride, m.p. 158° (38).]

[ $\bar{C}$  on chloromethylation with paraformaldehyde +  $HCl$  gas +  $H_3PO_4$  io  $AcOH$  gives (81) 1-chloro-4-(chloromethyl)naphthalene, m.p. 78-79° (81).]

[ $\bar{C}$  is not reduced with excess 5%  $Na/Hg$  io alc. eveo after 5 hrs. (39) nor by  $HI + P$  at 182° for 10 hrs. (42); however,  $\bar{C}$  in boilg.  $AmOH$  treated with  $Na$  yields (40) 1,4-dihydro-naphthalene [Beil. V-518,  $V_1$ -(249)] (identified by addn. of  $Br_2$  gviog dihydromide, m.p. 74° (40)) and 1,2,3,4-tetrahydro-naphthalene (1:7550) q.v.; furthermore,  $\bar{C}$  with  $Mg$  io boilg.  $MeOH$  evolves gas and upoo acidification and pouring into aq. gives alm. quoot. yield (41) naphthalene (1:7200), m.p. 80°.]

[ $\bar{C}$  on cat. oxido. with air at 250-300° gives (43) 97% phthalic anhydride (1:0725) + 3% 3-chlorophthalic anhydride (3:3900).]

[ $\bar{C}$  with  $Li$  in s.t. 17½ hrs. at 263° followed by treatment with aq. gives (44) naphthalene (1:7200) + 1,1'-binaphthyl [Beil. V-725,  $V_1$ -(358)], m.p. 156°. —  $\bar{C}$  with  $Li$  in dry ether yields soln. of  $\alpha$ -naphthyl-lithium which with  $Me_2SO_4$  gives (77% yield (45)) 1-methylnaphthalene (1:7600), the reactn. of  $\bar{C}$  with  $Li$  occurring even more readily (46) than with  $Mg$ .]

[ $\bar{C}$  with  $Mg$  at 200-220° reacts very eoegetically and is complete within a few minutes; naphthalene sublimes abundantly, and yield of  $\alpha$ - $C_{10}H_7MgCl$  is only 10-13% (47).]

[ $\bar{C}$  with  $AlCl_3$  at 100° gives small amts. (50) naphthalene (1:7200) + 2-chloronaphthalene (3:1285).]

[ $\bar{C}$  with  $CuCN$  io pyridioe htd. 24 hrs. in bath at 245-250° (92% yield (10)) or  $\bar{C}$  with  $K_4Fe(CN)_6$  + pyridioe at 270° for 18 hrs. (49) gives  $\alpha$ -naphthonitrile [Beil. IX-649, IX-1-(275)], h.p. 299° cor., b.p. 173-174° at 27 mm., 166-169° at 18 mm. (10).]

[ $\bar{C}$  does not with  $Ag$  3,5-dinitrobenzoate yield corresp. ester (80).]

[ $\bar{C}$  with 15% aq.  $NaOH$  above 300° for 12 hrs gives (46% yield (51))  $\alpha$ -naphthol (1:1500);  $\bar{C}$  with 5 moles 3-25% aq.  $NaOH$  at 350-360° uoder pressure in pres. of  $Cu$  for 1 hr. gives (52) a mixt. of  $\alpha$ -naphthol (1:1500) +  $\beta$ -naphthol (1:1540). —  $\bar{C}$  with aq.  $Na_2CO_3$  +  $Cu$  at 300° under press. (53) or  $\bar{C}$  with aq.  $Na_2CO_3$ ,  $Na_2HPO_4$ , or  $Na_2B_4O_7$  at 325° and 280 atm. (54) yields  $\alpha$ -naphthol (1:1500). —  $\bar{C}$  with aq. vapor over cat. at 300-400° yields (55)  $\alpha$ -naphthol (1:1500).]

[ $\bar{C}$  with conc. aq.  $NH_4OH$  +  $CuO$  at 150-250° under press. (56) or  $\bar{C}$  with conc. aq.  $NH_4OH$  +  $Cu_2Cl_2$  +  $Ca(OH)_2$  at 225-230° under press. (57) cf. (58) yields  $\alpha$ -naphthylamine (for study rate of reacto. see (58) (61); under suitable conditions the main prod. may be di- $\alpha$ -naphthylamine (60).]

[ $\bar{C}$  with  $KNH_2$  in liq.  $NH_3$  at -33° gives (82) only 2-3%  $\alpha$ -naphthylamine, the main prod. (43-53%) being  $\beta$ -naphthylamine; for behavior of  $\bar{C}$  with  $LiNEt_2$  see (83).]

[ $\bar{C}$  oo mononitration, e.g., with a mixt. of conc.  $HNO_3$  ( $D = 1.4$ ) (1 mole) + conc.  $H_2SO_4$  (2 moles) at 0° (63) cf. (64) (65) (66) gives a mixt. of three monoo nitro derivs., viz., 1-chloro-4-nitronaphthalene [Beil. V-555,  $V_1$ -(264)], pale yel. ndls. from alc., m.p. 85° (66) (63), 87-87.5° (67); 1-chloro-5-nitronaphthalene [Beil. V-556], m.p. 111° (63) (68); and 1-chloro-8-nitronaphthalene [Beil. V-556], ndls. from  $AcOH$  or  $C_6H_6$ , m.p. 94° (63), 93-94° (69). (Note that the relative proportions of these three mononitration products

[ $\bar{C}$  on htg. with Cu powder in  $C_6H_6$  for 25 hrs. gives (5) a mixt. of the two stereoisomeric forms of 1,2-bis-(*o*-chlorophenyl)-1,2-dichloroethylene, [Beil. V-635]; by repeated cryst. from pet. ether this mixt. is separable into 3 pts. higher-melting stereoisomer, m.p.  $172^\circ$  (5), and 1 pt. lower-melting stereoisomer, m.p.  $129^\circ$  (5).]

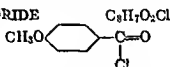
$\bar{C}$  on hydrolysis, e.g., by htg. with aq. in s.t. nt  $150^\circ$  (1) or by boildg. with conc.  $HNO_3$  (2), yields *o*-chlorobenzoic acid (3:4150) q.v.

3:6880 (1) Kolbe, Lautemann, Ann. 115, 183-185, 195-196 (1860). (2) Anschütz, Ann. 454, 95-99 (1927). (3) Meister Lucius Brüning, Ger. 229,873, Jan. 6, 1911, Cent. 1611, I 358. (4) Anschütz, Moore, Ann. 239, 321-322 (1887). (5) Fox, Ber. 20, 653-656 (1893). (6) Spreckels, Ber. 52, 319 (1919). (7) Wertyporoch, Ann. 493, 157-161 (1932). (8) Britton (to Dow Chem. Co.), U.S. 1,604,458, May 12, 1931; Cent. 1931, II 497; C.A. 25, 3668 (1931). (9) Kyrides (to Nat. Aniline and Chem. Co.), U.S. 1,733,268, Oct. 29, 1929; Cent. 1930, I 3831. (10) Soc. Chem. Ind. Basel, Ger. 355,115, June 21, 1922; Swiss. 92,406, Feb. 16, 1923; Cent. 1923, II 484.

(11) Soc. Chem. Ind. Basel, Ger. 378,908, Aug. 7, 1923; Ger. 378,909, Aug. 11, 1923; Swiss 98,559, April 2, 1923; Cent. 1923, IV 593. (12) Soc. Chem. Ind. Basel, Ger. 418,033, Aug. 26, 1925; Cent. 1925, II 2695. (13) Scottish Dyes, Ltd., Bangam, Thomas, Brit. 368,231, April 18, 1929; Cent. 1929, II 1348. (14) I.G., French 745,293, May 8, 1933; Cent. 1933, II 2961.

### 3:0800 4-METHOXYBENZOYL CHLORIDE

(*p*-Anisoyl chloride)



$C_8H_7O_2Cl$

Beil. X - 163

XI-(77)

B.P.

$202-203^\circ$  sl. dec.

(1)

M.P.

$24^\circ$

(7)

$D_4^{20} = 1.2009$  (6)  $n_D^{20} = 1.5802$  (6)

$202^\circ$

(9)

$22^\circ$

(4) (15)

$258.4-260.5^\circ$

(2)

$21^\circ$

(8)

$161-168^\circ$  at 38 mm. (3)

$160-164^\circ$  at 35 mm. (4)

$152-153^\circ$  at 24 mm. (4)

$148-153^\circ$  at 20 mm. (5)

$145^\circ$  at 14 mm. (4)

$137.6-137.8^\circ$  at 14 mm. (2)

$90.8^\circ$  at 1 mm. (6)

[For prepn. of  $\bar{C}$  from *p*-methoxybenzoic acid (*p*-anisic acid) (1:0805) with  $PCl_5$  (93% yield (3)) (4) (9) (10) (11) or with  $SOCl_2$  (6) (7) (12) (13) see indic. refs.; from sodium *p*-anisate with oxalyl chloride (3:5060) in  $C_6H_6$  (75-90% yield) see (14).]

[ $\bar{C}$  with 3%  $H_2O_2$  in acetone + pyridine nt  $0^\circ$  yields (15) di-*p*-anisyl peroxide, cryst. from AcOEt or pet. eth., m.p.  $128^\circ$  (15); for reactn. of  $\bar{C}$  with  $H_2S_2 + ZnCl_2$  giving (60% yield) di-*p*-anisyl disulfide see (30).]

[ $\bar{C}$  on cat. reductn. with  $H_2$  and cat. as directed gives (81% yield (16)) *p*-methoxybenzaldehyde (1:0240) (under some cond. (17) reductn. goes to *p*-methoxytoluene (methyl-*p*-tolyl ether) (1:7495)).]

[Although 2-methoxybenzoyl chloride (3:6870) with anhydrous  $Na_2CO_3$  + pyridine gives the corresp. anhydride, this reactn. is not specifically reported for  $\bar{C}$ ; however,  $\bar{C}$  + a tertiary amino (pyridine) in  $C_6H_6$  with excess  $K_2S_2O_8$  yields (18) *p*-methoxybenzoic acid anhydride, m.p.  $99-100^\circ$  (18).]

[ $\bar{C}$  with  $C_6H_6 + AlCl_3$  yields (1) *p*-methoxybenzophenone (1:5170);  $\bar{C}$  with toluene +  $AlCl_3$  gives (40% yield (11)) 4-methoxy-4'-methylbenzophenone, cryst. from alc., m.p.  $89^\circ$  (11);  $\bar{C}$  with perylene +  $AlCl_3$  in  $CS_2$  gives (19) 3,9-bis-(*p*-methoxybenzoyl)perylene, m.p.  $310.5^\circ$  (19).]

[ $\bar{C}$  condenses with many phenol ethers in pres. of  $AlCl_3$ ; e.g., for reactn. of  $\bar{C}$  with anisole

yielding 4,4'-dimethoxybenzophenone [Beil. VIII-317, VIII<sub>1</sub>-(641)], m.p. 143-144° (20), see (20) (21); for  $\bar{C}$  with phenetole yielding 4-methoxy-4'-ethoxybenzophenone, m.p. 112° (13), 111° (20), see indic. refs.; for  $\bar{C}$  with pyrocatechol dimethyl ether (veratrole) (1:7560) yielding 3,4,4'-trimethoxybenzophenone [Beil. VIII-422], m.p. 98-99°, see (22); for  $\bar{C}$  with resorcinol dimethyl ether (1:7570) yielding 2,4,4'-trimethoxybenzophenone [Beil. VIII<sub>1</sub>-(702)], m.p. 70-71° (23), see (23); for  $\bar{C}$  with phloroglucinol trimethyl ether (1:7148) yielding 2,4,6,4'-tetramethoxybenzophenone [Beil. VIII-496], m.p. 146°, see (22); for  $\bar{C}$  with many other phenol ethers see (20).]

[ $\bar{C}$  with MeZnI (24) or better with Me<sub>2</sub>Cd (25) gives (yields. 25% (24), 84% (25)) p-methoxyphenyl methyl ketone (p-methoxyacetophenone) (1:5140), m.p. 38°;  $\bar{C}$  with C<sub>6</sub>H<sub>5</sub>ZnBr gives (65% yield (26)) p-methoxybenzophenone, (1:5170), m.p. 61°, b.p. 202° at 14 mm. (26).]

[ $\bar{C}$  with ethyl sodioacetoacetate yields (4) ethyl  $\alpha$ -(p-methoxybenzoyl)acetoacetate [Beil. X-1004];  $\bar{C}$  with ethyl sodio- $\alpha,\gamma$ -dimethoxyacetoacetate yields (27) ethyl  $\alpha,\gamma$ -dimethoxy- $\alpha$ -(p-anisoyl)acetoacetate (which on ketonic hydrolytic cleavage yields (27)  $\omega$ ,4-dimethoxyacetophenone).]

[ $\bar{C}$  (1 mole) with HCN (4 moles) in dry ether + pyridine gives (12) p-methoxybenzoyl cyanide, m.p. 63°, b.p. 150° at 12 mm. (12);  $\bar{C}$  with KCN + quinoline yields (28) 1-(p-anisoyl)-2-cyano-1,2-dihydroquinoline, m.p. 120°, which upon acid hydrolysis gives (57% yield (28)) p-methoxybenzaldehyde (p-anisaldehyde) (1:0240).]

[ $\bar{C}$  with urea refluxed in C<sub>6</sub>H<sub>6</sub> for 15 hrs. yields (29) N-(p-methoxybenzoyl)urea, ndls. from alc., m.p. 215° (29).]

[For reactn. of  $\bar{C}$  with K<sub>2</sub>S in alc. + ether yielding K salt of p-methoxythiobenzoic acid see (30); for reactn. of  $\bar{C}$  with sodium phenylacetylene see (31); for reactn. of  $\bar{C}$  with diphenylketene see (32); for reactn. of  $\bar{C}$  with d-glucose and other carbohydrates see (33); for reactn. of  $\bar{C}$  with 3,4-dimethoxyphenylethylamine (34) or with  $\beta$ -(n-butylamino)ethanol (3) see indic. refs.]

$\bar{C}$  with MeOH yields methyl p-methoxybenzoate (methyl p-anisate) (1:2128), m.p. 49°;  $\bar{C}$  with EtOH yields ethyl p-anisate (1:4191), b.p. 269°, m.p. +7° (for study of rate of reactn. of  $\bar{C}$  with EtOH see (3) (35)).

$\bar{C}$  on hydrolysis yields p-methoxybenzoic acid (1:0805), m.p. 184°; for the amide, anilide, p-toluidide, and other derivs. corresp. to  $\bar{C}$  see p-methoxybenzoic acid (1:0805).

3:6890 (1) Ullmann, Goldberg, *Ber.* 35, 2814 (1902). (2) Kohlrausch, Pongratz, Stockmair *Monatsh.* 67, 110 (1935). (3) Pierce, Salisbury, Fredericksen, *J. Am. Chem. Soc.* 64, 1691-1694 (1942). (4) Schoonjans, *Bull. acad. roy. Belg.* (3) 33, 810-820 (1897), *Cent.* 1897, II 616. (5) de Ceuster, *Natuurw. Tijdschr.* 14, Nos 3-6, 188-202 (1932), *Cent.* 1932, II 1296. (6) Thompson, Norris, *J. Am. Chem. Soc.* 58, 1956 (1936). (7) Meyer, *Monatsh.* 22, 428 (1901). (8) Branch, Nixon, *J. Am. Chem. Soc.* 59, 2499-2504 (1936). (9) Cahours, *Ann. chim.* (3) 23, 350-354 (1848); *Ann.* 70, 47-48 (1849). (10) Lossen, *Ann.* 175, 284, Note (1875).

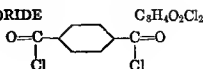
(11) Orzechow, Brouty, *Bull. soc. chim.* (4) 47, 623 (1930). (12) Marsh, Stephen, *J. Chem. Soc.* 127, 1635 (1925). (13) Schönbarg, Schütz, Nickel, *Ber.* 61, 1380 (1927). (14) Adams, Uhlich, *J. Am. Chem. Soc.* 42, 608 (1920). (15) Vanino, Uhlfelder, *Ber.* 37, 3624 (1904). (16) Rosenmund, *Zetsche, Ber.* 56, 1483 (1923). (17) Rosenmund, *Zetsche, Ber.* 54, 641 (1921). (18) Gasopoulos, *Praktika Akad. Athenon* 6, 347-353 (1931); *Cent.* 1932, I 3172. (19) Zinke, Funke, *Ber.* 58, 2225 (1925). (20) Jones, *J. Chem. Soc.* 1936, 1860.

(21) Schnackenberg, Schell, *Ber.* 36, 654 (1903). (22) von Kostanecki, Tambor, *Ber.* 39, 4024, 4026 (1906). (23) Ziegler, Ochs, *Ber.* 55, 2273 (1922). (24) Mauthner, *J. prakt. Chem.* (2) 103, 392, 396 (1922). (25) Gilman, Nelson, *Rec. trav. chim.* 55, 528-529 (1936). (26) Martynoff, *Ann. chim.* (11) 7, 439 (1937). (27) Pratt, Robinson, *J. Chem. Soc.* 127, 169 (1925). (28) Sugawara, Tsuda, *J. Pharm. Soc. Japan*, 56, 103-105 (1936); *Cent.* 1936, II 3670. (29) Kaufmann, *Arch. Pharm.* 265, 236 (1927). (30) Block, Bergmann, *Ber.* 53, 974-975 (1920).

(31) Weygand, Bauer, *Ann.* 459, 141 (1927). (32) Staudinger, Kon. *Ann.* 354, 117 (1911). (33) Oden, *Arkiv Kemi, Mineral. Geol.* 7, No 16, 1-16 (1915), *Cent.* 1923, III 254-256; *C.A.* 14, 2171 (1920). (34) Ahluwalia, Narang, *Ray, J. Chem. Soc.* 1931, 2058. (35) Norris, Fasce, Staud, *J. Am. Chem. Soc.* 57, 1415-1420 (1935).



## — TEREPTHALYL (DI)CHLORIDE

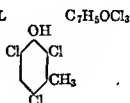

 Beil. IX<sub>1</sub>- 844  
 IX<sub>1</sub>-(376)

B.P. 263°

M.P. 83°

See 3:2205. Division A: Solids.

## — 2,4,6-TRICHLORO-3-METHYLPHENOL


 Beil. VI —  
 VI<sub>1</sub>—  
 VI<sub>2</sub>-(356)

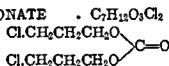
B.P. 265°

M.P. 46°

See 3:0618. Division A: Solids.

## 3:6895 DI-(γ-CHLOROPROPYL) CARBONATE

(γ,γ-Dichloropropyl carbonate)

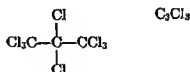

 Beil. III —  
 III<sub>1</sub>—  
 III<sub>2</sub>-(5)

B.P. 265–270° at 740 mm. (1)

[Obtd. as by-product in prepn. of γ-chloropropyl chloroformate (3:6010) from phosgene and trimethylene chlorohydrin (3:8285) (1).]

3:6895 (1) Pierce, Adams, *J. Am. Chem. Soc.* 45, 791–792 (1923).

## — OCTACHLOROPROPANE

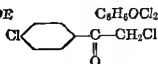

 Beil. I - 108  
 I<sub>1</sub>-( 35)  
 I<sub>2</sub>—

B.P. 268–269° at 734 mm.

M.P. 160° (7)

See 3:4450. Division A: Solids.

## — p-CHLOROPHENACYL CHLORIDE

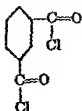

 Beil. VII - 282  
 VII<sub>1</sub>-(152)

B.P. 270°

M.P. 101–102°

See 3:2990. Division A: Solids.

— ISOPHTHALYL (DI)CHLORIDE

 $C_8H_4O_2Cl_2$ Beil. IX - 834  
IX<sub>1</sub>-(372)

B.P. 276° M.P. 43°

See 3:0520. Division A: Solids.

— 3,4,5-TRICHLOROPHENOL

 $C_6H_3OCl_3$ 

Beil. VI —

VI<sub>1</sub>—VI<sub>2</sub>-(181)

B.P. 271-277° u.c. at 745 mm.

M.P. 101°

See 3:2835. Division A: Solids.

— PENTACHLOROBENZENE

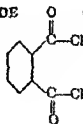
 $C_6HCl_5$ 

Beil. V - 205

V<sub>1</sub>-(113)V<sub>2</sub>-(157)

B.P. 276-277° M.P. 86-87°

See 3:2290. Division A: Solids.

3:6900 *sym.-o*-PHTHALYL DICHLORIDE  
(*sym.-o*-Phthaloyl dichloride) $C_8H_4O_2Cl_2$ 

Beil. IX - 805

IX<sub>1</sub>-(363)

B.P.		M.P.			
276.7°	at 760 mm. (1)	16°	(7)	$D_4^{20} = 1.4089$	(2)
275.4°	at 726 mm. (2)	15-16°	(1) (5)	1.4060	(6)
269-270°	(3)	13°	(5)	$n_D^{20} = 1.5692$	(6)
156-157°	at 23 mm. (4)	11.5-12°	(6)		1.56919 (2)
150° cor.	at 23 mm. (5)	11-12°	(7)	$D_4^{15.5} = 1.4077$	(4)
153.3-153.7°	at 22 mm. (6)			$n_D^{15.5} = 1.57099$	(4)
131-133°	at 9-10 mm. (7)				

[See also *unsym.-o*-phthalyl dichloride (3:2395).]

The m.p. of ord. samples of  $\bar{C}$  is usually abt. 12°, but distn. at ord. press. (7) yields a prod. with m.p. 16°. The chem. of  $\bar{C}$  is closely connected with that of the isomeric *unsym.-o*-phthalyl dichloride (3:2395) q.v.; for f.p./compn. curve for mixts. of the two isomers see (8).

[For prepn. of  $\bar{C}$  from phthalic anhydride (1:0725) with  $PCl_5$  (92% yield (7)) (1) (3) (9) (10), with  $PCl_3 + Cl_2$  (12), with benzotrichloride (3:6540) + a little  $ZnCl_2$  (13), with a little  $ZnCl_2$  at  $220^\circ$  by grad. addn. of  $SOCl_2$  (100% yield (14)) (15), or with  $CCl_4$  (etc.) + 2%  $ZnCl_2$  at  $250-280^\circ$  (16) see indic. refs.; from phthalic acid (1:0820) with benzotrichloride + a little  $ZnCl_2$  see (17).]

[For prepn. of  $\bar{C}$  from unsym.-o-phthalyl dichloride (3:2395) by htg. at  $150^\circ$  for 1 hr. see (5); from thiophthalic anhydride [Beil. XVII-486, XVII-1-(256)] with dry  $Cl_2$  at  $245^\circ$  see (18); for formn. as by-product of action of  $Cl_2$  on o-toluoyl chloride (3:8740) see (19).] [For purification of  $\bar{C}$  by treatment with  $MgO$  or  $CaO$  see (20).]

$\bar{C}$  on htg. with  $AlCl_3$  ( $\frac{1}{2}$  mole), then decg. cpd. with aq. and extracting with pet. ether, isomerizes (72% yield (7)) (1) (21) to unsym.-o-phthalyl dichloride (3,3-dichlorophthalide) (3:2395), m.p.  $89^\circ$ .

[ $\bar{C}$  with  $Cl_2$  at  $120-170^\circ$  in pres. of  $Fe$  yields (22) tetrachlorophthalic acid (3:4946).]

[ $\bar{C}$  on reduction with  $Zn + HCl$  (23) (24) or  $HI + P$  in  $CS_2$  (23) (25) yields phthalide (1:4920);  $\bar{C}$  on boilg. with  $AcOH + Na/Hg$  yields (26) phthalyl alcohol (o-xylylene glycol) [Beil. VI-910].]

$\bar{C}$  on heating with  $K$  in xylene (27), or with *ter*-bases +  $K_2S_2O_8$  (28), or with  $ZnCl_2 + SO_2$  at  $200^\circ$  (14) yields phthalic anhydride (1:0725). [Note that last reaction is the reverse of an impt. method (15) of prepa. of  $\bar{C}$ .]

[ $\bar{C}$  on shaking for 20 min. at  $60^\circ$  in glass flask with  $ZnF_2$ , then extracting with pet. eth. yields (29) o-phthalyl difluoride, m.p.  $42-43^\circ$ , h.p.  $224-236^\circ$  at 760 mm. (29);  $\bar{C}$  with  $HBr$  gas at  $150-160^\circ$  gives (50% yield (30)) sym.-o-phthalyl dihydromide, m.p.  $78-81^\circ$  rap. htg., h.p.  $191^\circ$  at 24 mm.,  $134^\circ$  at 2 mm. (30).]

[ $\bar{C}$  htd. with a little  $ZnCl_2$  and diethyl ether (31) or diethyl phthalate (32) gives (80% yield (31)) ethyl chloride (3:7015).] [Use in mfg. of alkyl chlorides (33).]

[For reactn. of  $\bar{C}$  with glycols see (34); for use of  $\bar{C}$  in acylation of cellulose see (35).]

[For behavior of  $\bar{C}$  with  $H_2O_2$  yielding phthalyl peroxide see (36); with  $PCl_5$  see (37); with  $NaN_3$  see (38) (39); with  $C_6H_5MgBr$  see (40).]

$\bar{C}$  on treatment with cold conc.  $NH_4OH$  followed by acidification yields (41) (42) o-cyanobenzoic acid [Beil. IX-814, IX-1-(365)], m.p.  $190^\circ$  dec., converted by htg. to phthalimide, m.p.  $228.5^\circ$  u.e. [For reactn. of  $\bar{C}$  with dimethylamine yielding  $N,N,N',N'$ -tetramethyl-o-phthalaldiamide, m.p.  $121-122^\circ$ , see (43); with diethylamine yielding (44) (45) corresp.  $N,N,N',N'$ -tetra-ethyl-o-phthalaldiamide, m.p.  $36^\circ$  (44),  $39^\circ$  (45) see indic. refs.]

$\bar{C}$  htd. with 1 mole acetamide until no more  $HCl$  is evolved gives in good yield (46) *N*-acetylphthalimide, cryst. from toluene, m.p.  $135-136^\circ$  (46); similarly benzamide gives *N*-benzoylphthalimide, m.p.  $168^\circ$  (46).

$\bar{C}$  reacts instantly with aniline yielding (29) sym.-phthalaldianilide, m.p.  $253-255^\circ$ . [Note that when  $\bar{C}$  is treated with aniline in ether or  $C_6H_6$  and stood for some time the prod. has m.p. about  $231^\circ$ ; when recrystd. from  $EtOH$ , however, the m.p. rises to  $253-255^\circ$ . This apparent anomaly is attributable to the pres. in most samples of  $\bar{C}$  of some phthalic anhydride whose slower reactn. with aniline contaminates the main prod. but is removed by recrystn. from alc. If, on reactn. of ord.  $\bar{C}$  with aniline, the resultant ppt. is filtered at once (before the anhydride has reacted), washed with  $C_6H_6$ , alc., and then aq., the prod. shows m.p.  $253-255^\circ$  without recrystn. (29).]

$\bar{C}$  on hydrolysis yields o-phthalic acid (1:0825) q.v.

3:6900 (1) Ott, *Ann.* 392, 273-277 (1912). (2) Brühl, *Ann.* 235, 13-14 (1886). (3) Claus. Hoch, *Ber.* 19, 1187-1194 (1886). (4) von Auwers, Schmidt, *Ber.* 46, 483 (1913). (5) Garner. Sugden, *J. Chem. Soc.* 1927, 2878, 2881. (6) Martin, Partington, *J. Chem. Soc.* 1936, 1181. (7) Ott, *Org. Syntheses*. Coll. Vol. 2 (1st ed.), 528-530 (1943); 11, 88-91 (1931). (8) Csanyi. *Monatsh.* 40, 81-92 (1919). (9) Auger, *Ann. chim.* (6) 22, 295-302 (1891). (10) Tingle, Cram, *Am. Chem. J.* 37, 603-604 (1907).

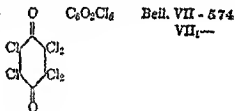
{11} Graebe, *Ann.* 238, 329 Note (1887). {12} Clemmensen, Miller (to Monsanto Chem. Co.), U.S. 1,974,845, Sept. 25, 1934; *Cent.* 1935, I 960; *C.A.* 28, 7265 (1934). {13} Kyrides (to Monsanto Chem. Co.), U.S. 1,963,749, June 19, 1934, *Cent.* 1934, II 2900; *C.A.* 28, 5079 (1934). {14} Kyrides, *J. Am. Chem. Soc.* 59, 206-208 (1937). {15} Kyrides (to Monsanto Chem. Co.), U.S. 1,951,364, Mar. 20, 1934; *Cent.* 1934, II 333; *C.A.* 28, 3424 (1934). {16} Mares (to Monsanto Chem. Co.), U.S. 2,051,096, Aug. 18, 1936, *Cent.* 1936, II 3591, *C.A.* 30, 6762 (1936). {17} Kyrides (to Monsanto Chem. Co.), U.S. 1,963,748, June 19, 1934; *Cent.* 1934, II 2900; *C.A.* 28, 5080 (1934). {18} Ott, Langenohl, Zerweck, *Ber.* 70, 2360-2362 (1932). {19} Davies, Perkin, *J. Chem. Soc.* 121, 2213 (1922). {20} Luthy, Thomas (to Monsanto Chem. Works), U.S. 1,906,761, May 2, 1933; *C.A.* 27, 3484 (1933), *Brit.* 397,775, Sept. 21, 1933; *Cent.* 1933, II 3194.

{21} Scheiber, *Ber.* 46, 2366-2370 (1913). {22} Zalkind, Belikova, *Russ.* 35,188, Mar. 31, 1934; *Cent.* 1935, II 1090; *C.A.* 30, 3443 (1936). {23} Hessert, *Ber.* 10, 1445-1447 (1877). {24} Hessert, *Ber.* 11, 238-239 (1878). {25} Baeyer, *Ber.* 10, 123-124 (1877). {26} Hessert, *Ber.* 12, 646-648 (1879). {27} Pearl, Evans, Dehn, *J. Am. Chem. Soc.* 60, 2470 (1938). {28} Gasopoulos, *Praktika Akad. Athnon.* 6, 347-353, *Cent.* 1932, I 3172. {29} Dann, Davies, Hambly, Paul, Semmens, *J. Chem. Soc.* 1933, 17. {30} Davies, Hambly, Semmens, *J. Chem. Soc.* 1933, 1309-1315.

{31} Kyrides, *J. Am. Chem. Soc.* 55, 1209-1212 (1933). {32} Kyrides, Dvornikoff, *J. Am. Chem. Soc.* 55, 4630-4632 (1933). {33} Kyrides (to Monsanto Chem. Co.), U.S. 1,939,216, Dec. 12, 1933; *Cent.* 1934, I 2040, *C.A.* 28, 1361 (1934). {34} Carothers, Arvin, *J. Am. Chem. Soc.* 51, 2560-2570 (1929). {35} *Brit.* 319,584, Nov. 20, 1929, *Cent.* 1930, I 1377. {36} McKee, U.S. 1,614,037, Jan. 11, 1927, *Brit.* 271,725, June 23, 1927, *Cent.* 1927, II 1085, *C.A.* 21, 745 (1927). {37} Ott, *Ber.* 55, 2108-2125 (1922). {38} Darapsky, Gaudian, *J. prakt. Chem.* (2) 147, 47-48 (1930). {39} Lindemann, Schultheis, *Ann.* 464, 249-253 (1928). {40} Clar, St. John, Hawran, *Ber.* 67, 940-950 (1929).

{41} Hoogewerff, van Dorp, *Rec. trav. chim.* 11, 91-94 (1892). {42} Scheiber, Knothe, *Ber.* 45, 2252-2255 (1912). {43} von Braun, Kaiser, *Ber.* 55, 1307-1310 (1922). {44} Maxim, *Compt. rend.* 184, 690 (1927). {45} French 785,428, Aug. 9, 1935, *Cent.* 1935, II 3441; *C.A.* 30, 488 (1936). {46} Evans, Dehn, *J. Am. Chem. Soc.* 51, 3652 (1929).

— 2,3,5,6,6-HEXACHLOROCYCLOHEXEN-2-DIONE-1,4

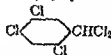


B.P. 275-285° dec.

M.P. 89°

See 3:2360. Division A: Solids.

3:6910 2,4,5-TRICHLOROBENZAL (DI)CHLORIDE  $C_7H_3Cl_5$  Beil. V - 303  
(2,4,5-Trichlorobenzylidene (di)chloride)  $V_1$ -(153)  
 $V_2$ —



B.P. 280-281° (1)

$D_{25}^{20} = 1.607$  (1)

Oil which below 0° solidifies to colorless cryst.

[For prepn. of  $\bar{C}$  from 2,4,5-trichlorotoluene (3:2100) at b.p. with  $Cl_2$  see (1); for formn. of  $\bar{C}$  from toluene in  $AcOH/HCl$  on electrolysis in dark see (6).]

$\bar{C}$  on hydrolysis with fuming  $H_2SO_4$  {2}, warm conc.  $H_2SO_4$  {3}, or with aq. in s.t. at 260° {4} (1) gives 2,4,5-trichlorobenzaldehyde (3:3375).

[For use of  $\bar{C}$  in prepn. of dyestuffs see (5).]

3:6910 (1) Beilstein, Kuhlberg, *Ann.* 150, 299 (1869). (2) Seelig, *Ann.* 237, 149-149 (1887). (3) Fischer, *Ger.* 25,827; June 23, 1883; *Friedländer* 1, 42 (1877-87). (4) Beilstein, Kuhlberg, *Ann.* 152, 238-239 (1869). (5) Schmidlin (to Cassella and Co.), *Ger.* 363,290, Nov. 6, 1922; *Cent.* 1923, II 482; not in *C.A.* (6) Fichter, Glantzstein, *Ber.* 49, 2484 (1916).

## — 2,6-DICHLORONAPHTHALENE

 $C_{10}H_8Cl_2$ 

Beil. V - 544

V<sub>1</sub>—V<sub>2</sub>-(446)

B.P. 285° u.c.

M.P. 136°

See 3:4040. Division A: Solids.

— 1,7-DICHLORONAPHTHALENE  
(2,8-Dichloronaphthalene) $C_{10}H_8Cl_2$ 

Beil. V - 543

V<sub>1</sub>-(263)V<sub>2</sub>-(446)

B.P. 286° u.c.

M.P. 63.5-64.5°

See 3:1385. Division A: Solids.

## — 1,4-DICHLORONAPHTHALENE

 $C_{10}H_8Cl_2$ 

Beil. V - 542

V<sub>1</sub>-(262)V<sub>2</sub>-(445)

B.P. 286-287° at 740 mm.

M.P. 68°

See 3:1655. Division A: Solids.

## — 1,3-DICHLORONAPHTHALENE

 $C_{10}H_8Cl_2$ 

Beil. V - 542

V<sub>1</sub>-(262)V<sub>2</sub>-(445)

B.P. 291° cor. at 775 mm.

M.P. 61-62°

See 3:1310. Division A: Solids.

## — 1,2-DICHLORONAPHTHALENE

 $C_{10}H_8Cl_2$ 

Beil. V - 542

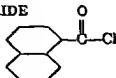
V<sub>1</sub>-(262)V<sub>2</sub>-(445)

B.P. 295-298°

M.P. 34-35°

See 3:0320. Division A: Solids.

## 3:6930 α-NAPHTHOYL CHLORIDE

 $C_{11}H_7OCl$ 

Beil. IX - 648

IX<sub>1</sub>-(275)

B.P.

M.P.

297.5°

(1)

26° (7)

182-183° at 14 mm.

(2)

22° (5)

172-173° at 15 mm.

(3) (4)

20° (3) (9)

107-108° at 15 mm.

(11)

158° at 12 mm.

(5)

168° at 10 mm.

(6)

163° at 10 mm.

(7) (8)

[For prepn. of  $\bar{C}$  from  $\alpha$ -naphthoic acid (1:0785) with  $PCl_5$  (yield: 100% (4) (8)) (6) (1) (11) in  $CCl_4$  (10) or with  $SOCl_2$  (12) (13) (14) (7) see indic. refs.]

$\bar{C}$  + anhyd.  $Na_2CO_3$  + pyridine treated with a few drops of aq. (14), or  $\bar{C}$  with various  $RMgX$  or other organometallic cpds. (15), or  $\bar{C}$  htd. with Ca  $\alpha$ -naphthoate (1), gives (80% yield (14))  $\alpha$ -naphthoic acid anhydride, pr. from  $C_6H_6$ , m.p. 145-146° (1) (14) (15).

[ $\bar{C}$  on cat. hydrogenation gives (33% yield (5))  $\alpha$ -naphthaldehyde [Beil. VII-400, VII<sub>1</sub>- (212)], b.p. 173-174° at 35 mm. (*p*-nitrophenylhydrazones, m.p. 233-235° (5)).]

[ $\bar{C}$  with  $AlCl_3$  + hydrocarbons give corresp.  $\alpha$ -naphthyl ketones: e.g., with  $C_6H_6$  (6), biphenyl (8),  $\alpha$ -methylnaphthalene (16),  $\beta$ -methylnaphthalene (17) (18), with 2,3- (19), 2,6- and 2,7- (20) dimethyl-naphthalenes, with various subst. perylenes (21) (22), see indic. refs.;  $\bar{C}$  with  $RMgX$  cpds. also yields corresp.  $\alpha$ -naphthyl ketones. e.g., with  $\alpha$ -naphthyl  $MgBr$  (14) or  $\alpha$ -tetralyl  $MgBr$  (23), see indic. refs.]

$\bar{C}$  with aq. hydrolyzes very slowly (9) yielding  $\alpha$ -naphthoic acid (1:0785) m.p. 161-162°. — For the amide, anilide, and other deriva. corresp. to  $\bar{C}$  see  $\alpha$ -naphthoic acid (1:0785); in addition to these see below

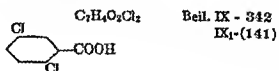
①  $\alpha$ -Naphthoic  $\beta$ -naphthalide: cryst. from alc., m.p. 200° (13) [From  $\bar{C}$  +  $\beta$ -naphthylamine in  $C_6H_6$  (13).]

3:6930 (1) Hofmann, *Ber.* 1, 41-42 (1865). (2) Bergmann, Schuchardt, *Ann.* 437, 253 (1931). (3) Linnell, Rouahdi, *Quart. J. Pharm. Pharmacol.* 14, 270-280 (1941). (4) von Braun, *Ber.* 38, 180 (1905). (5) Shoosmith, Guthrie, *J. Chem. Soc.* 1928, 2332. (6) Reddeken, *Ber.* 46, 2722. Note 2 (1913). (7) Bell, *J. Chem. Soc.* 1930, 1984-1985. (8) Schmidlin, Garcia-Banus, *Ber.* 45, 3183 (1912). (9) Pope, Winmill, *J. Chem. Soc.* 1912, 2316 (1912). (10) West, *J. Am. Chem. Soc.* 42, 1662 (1920).

(11) Sperl, Herzhaft, *Roczniki Chem.* 14, 1238-1242 (1934), *Cent.* 1935, I 2530. (12) Stollé, *J. prakt. Chem.* (2) 74, 19 (1906). (13) Beckmann, Liesche, Correns, *Ber.* 56, 354 (1923). (14) Blicke, *J. Am. Chem. Soc.* 49, 2847-2848 (1927). (15) Bruce, *J. Am. Chem. Soc.* 60, 2277 (1938). (16) Cook, Robinson, *J. Chem. Soc.* 1933, 510. (17) Clar, *Ber.* 62, 355-356 (1929). (18) French 614,959, Dec. 27, 1926; *Cent.* 1929, II 796. (19) Cook, *J. Chem. Soc.* 1933, 1596. (20) Cook, *J. Chem. Soc.* 1932, 492.

(21) Zinke, Funke, *Ber.* 58, 2222-2227 (1925). (22) French 589,643, June 2, 1925; *Cent.* 1926, I 1053. (23) Fieser, Seligman, *J. Am. Chem. Soc.* 58, 478-480 (1936).

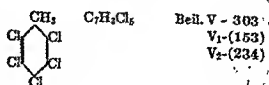
#### — 2,5-DICHLOROBENZOIC ACID



B.P. 301°      M.P. 155°

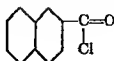
See 3:4340. Division A: Solids.

#### — 2,3,4,5,6-PENTACHLOROTOLUENE



B.P. 301°      M.P. 224-225°

See 3:4937. Division A: Solids.

—  $\beta$ -NAPHTHOYL CHLORIDE $C_{11}H_7OCl$ Beil. IX - 657  
IX<sub>1</sub>—

B.P. 304–306°

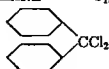
M.P. 51°

See 3:0900. Division A: Solids.

3:6960  $\alpha,\alpha$ -DICHLORODIPHENYLMETHANE $C_{13}H_{10}Cl_2$ 

Beil. V - 590

(Benzophenone (di)chloride;

 $\alpha,\alpha$ -dichloroditan)V<sub>1</sub>-(278)V<sub>2</sub>-(501)

B.P.

305° cor. dec. (1)

 $D_{18}^{25} = 1.235$  (1)

220° at 671 mm. (1)

235° at 70 mm. (2)

201–202° at 35 mm. (3) (4) (15)

103° at 30 mm. (5) (10)

186° at 26 mm. (6)

189–190° at 21 mm. (7)

172° at 16 mm. (8)

165° at 12 mm. (23)

Colorless oil showing bluish fluorescence and having only faint odor (3).

[For prepn. of  $\bar{C}$  from benzophenone (1:5150) with  $PCl_5$  (yield: 90% (3), 85% (7), 68% (9)) (1) (10) (11) (12) (15); with  $PCl_5$  in  $C_6H_6$  (92% yield (13)), or with oxalyl dichloride (3:5060) in s.t. at 130–140° (14) see indic. refs.; from  $C_6H_6 + AlCl_3 +$  excess  $CCl_4$  (yield: 90–95% (16), 80–90% (18)) (17) see indic. refs.; for formn. of  $\bar{C}$  from diphenylmethane (1:7120) with  $PCl_5$  in s.t. at 170° see (13), from *bis*-(triphenylmethyl) peroxide with  $PCl_5$  (19) or with  $Cl_2$  in  $CCl_4$  in pres. of  $I_2$  (19), from diphenyldiazomethane with  $SOCl_2$  or  $SO_2Cl_2$  in pet. ether (100% yield (20)), or from benzotrichloride (3:6540) htd. with uranium metal at 115–128° (4) see indic. refs.]

[For use of  $\bar{C}$  in prepn. of acid anhydrides by htg. at 110–120° with salts of aliph. or arom. acids see (21).]

$\bar{C}$  hydrolyzes slowly with cold but rapidly with hot aq. yielding (1) benzophenone (1:5150) and  $HCl$  (for study of rate of hydrolysis of ether soln. on shaking with aq. see (22));  $\bar{C}$  dis. in conc.  $H_2SO_4$  with yel. color (which grad. disappears) and on pouring onto ice yields (6) benzophenone (1:5150);  $\bar{C}$  in dry ether shaken 2 hrs. with silver oxide gives (78% yield (23)) benzophenone (1:5150);  $\bar{C}$  with alc.  $NH_3$  yields (33) benzophenone.

$\bar{C}$  with  $MeOH$  alone (6), with dry  $MeOH + Mg$  (24), with dry  $MeOH$  in dry pyridine at 0° (25), with  $NaOMe$  in  $MeOH$  (3) (26), or with  $NaN_3$  in dry  $MeOH$  (27) gives (yields: 86% (6) (24), 81% (3))  $\alpha,\alpha$ -dimethoxy-diphenylmethane (benzophenone dimethylacetal) [Beil. VII-415], cryst. from  $MeOH$ , m.p. 107–108° (25), 107.5° cor. (24), 106.5–107° (3) (for application to higher alcs. see (3) (26)).

$\bar{C}$  htd. with  $Ag$  (11) (5), or stood overnight with  $Ag$  or  $Zn$  in dry  $EtOAc$  (28) cf. (29), or reflux in  $CS_2$  with 3–4 moles  $Hg$  (28) (less  $Hg$  gives different result), or with 2 moles  $NaI$  in boilg. acetone (30) (1 mole  $NaI$  gives different result), or with excess cyclohexyl- $MgBr$  (31) (less reagent gives different result), or with  $Na$  in liq.  $NH_3$  (90% yield (32)) or htd. 8 hrs. with diphenylmethane (1:7120) (83% yield (12)) gives tetraphenylethylene [Beil. V-743, V<sub>1</sub>-(376)], m.p. 227° cor., 222° u.c. (31), 221° (11). — [ $\bar{C}$  does not react with

Mg in dry ether even in pres. of  $I_2$  (28).] — [ $\bar{C}$  refluxed in  $CS_2$  with less than 3 moles Hg (28), or  $\bar{C}$  with 1 mole NaI in acetone in cold (30), or  $\bar{C}$  with 1 mole cyclohexyl MgBr (31), gives tetraphenylethylene dichloride (Beil. V<sub>1</sub>-(371)), cryst. from ether, m.p. 186° cor. dec. (31).]

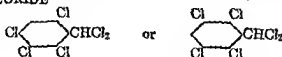
[ $\bar{C}$  with 2 moles Ag azide in ether gives (88% yield (34)) benzophenone diazide, m.p. 42°;  $\bar{C}$  treated as directed (15) with alc. NaSH gives 42-50% yield thiobenzophenone (Beil. VII-429, VII<sub>1</sub>-(232)), cryst. from pet. ether, m.p. 53-54° (15) (note that an excess of  $\bar{C}$  must always be present to prevent reduction of the thiobenzophenone to dibenzohydril disulfide (Beil. VI-681), ndls. from alc., m.p. 152°, and that the latter is obtd. in 70% yield (15) if  $\bar{C}$  is added to the alc. NaSH instead of the reverse); for reactn. of  $\bar{C}$  with diethyl sodio-malonate (2) (9) or with ethyl sodioacetoacetate (8) see indic. refs.; for reaction of  $\bar{C}$  with  $SbF_3$  yielding  $\alpha,\alpha$ -difluorodiphenylmethane, b.p. 260° dec., 125° at 10 mm., m.p. -1.8°,  $D_4^{20} = 1.1614$ ,  $n_D^{20} = 1.53786$ , see (35)]

$\bar{C}$  with 4 moles aniline in cold gives (36) benzophenone anil (Beil. XII-201, XII<sub>1</sub>-(174)) + aniline hydrochloride, the former is sol. in ether, the latter in aq.; sepn. of the layers and addition of alc. to the ether ppts. benzophenone anil, pale yel. lfts. from abs. alc., m.p. 109° u.c. (36) 113°.

3:6960 (1) Kekulé, Franchimont, *Ber* 5, 908-909 (1872). (2) Phalnikar, Nargund, *J. Univ. Bombay* 5, F (1935). (3) Mackenzie, *J. Chem. Soc.* (1935). (4) Anschütz, *Ann.* (1935). (5) Anschutz, *Ann.* (1935). (6) Hsu, Ingold, *Wilson, J.* (1935). (7) Adickes, *J. prakt. Chem.* (2) 145, 239 (1936). (8) Gattermann, Schulze, *Ber* 29, 2944-2945 (1896). (9) Behr, *Ber* 3, 752 (1870). (10) Norris, Thomas, Brown, *Ber* 43, 2958-2959 (1910). (11) Cone, Robinson, *Ber* 40, 2161-2162 (1907). (12) Staudinger, *Ber* 42, 3976 (1909). (13) Staudinger, *Ber* 42, 3976 (1909). (14) Staudinger, *Ber* 42, 3976 (1909). (15) Staudinger, *Ber* 42, 3976 (1909). (16) Staudinger, *Ber* 42, 3976 (1909). (17) Riddell, Noller, *J. Am. Chem. Soc.* 24, 1-3 (1905). (18) Pfenninger, *Ber* 49, 1941 (1916).

(19) Staudinger, *Clar, Czako, Ber* 44, 1644 (1911). (20) Finkelstein, *Ber* 43, 1532-1533 (1910). (21) Schmidlin, von Escher, *Ber* 45, 894-895 (1912); 43, 1157, 1159 (1910). (22) Dean, Berchet, *J. Am. Chem. Soc.* 52, 2825 (1930). (23) Pauly, *Ann.* 187, 217-220 (1877). (24) Götzky, *Ber* 64, 1558 (1931). (25) Henne, Leicester, *J. Am. Chem. Soc.* 60, 864-865 (1938). (26) Ref. 33, pp. 199-202.

3:6980 2,3,4,6-(or 2,3,5,6)-TETRACHLOROBENZAL  $C_6H_2Cl_4$  Beil. V - 303  
(DI)CHLORIDE  $V_1$ -(153)  
 $V_2$ —



B.P. 305-306° (1)

$D_4^{25} = 1.704$  (1)

[For prepn of  $\bar{C}$  from 2,3,4,6-tetrachlorotoluene (3:2480) or from 2,3,5,6-tetrachlorotoluene (3:2575) at their b.p.'s with  $Cl_2$  (1) or with  $Cl_2$  at 100-130° (especially in light from Hg-vapor lamp) (2) see indic. refs.]

$\bar{C}$  with strong  $H_2SO_4$  at 90° is hydrolyzed (2) to 2,3,4,6-(or 2,3,5,6)-tetrachlorobenzaldehyde (3:2700).

3:6980 (1) Beilstein, Kuhlberg, *Ann.* 150, 303-304 (1869). (2) Cassella and Co., *Ger.* 290, 209, Feb. 8, 1916; *Cent* 1916, I 396-397; not in C.A.



## — PENTACHLOROPHENOL



Beil. VI - 194

VI<sub>1</sub>-(104)VI<sub>2</sub>-(182)

B.P. 309-310° at 764 mm.

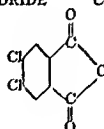
M.P. 190°

*See 3:4850. Division A: Solids.*

## — 4,5-DICHLOROPHTHALIC ANHYDRIDE



Beil. XVII - 483

XVII<sub>1</sub>-(254)

B.P. 313°

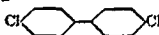
M.P. 187-188°

*See 3:4830. Division A: Solids.*

## — 4,4'-DICHLOROBIPHENYL



Beil. V - 579

V<sub>1</sub>-(273)V<sub>2</sub>-(484)

B.P. 315°

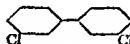
M.P. 148°

*See 3:4200. Division A: Solids.*

## — 3,3'-DICHLOROBIPHENYL



Beil. V - 579

V<sub>1</sub>-(272)V<sub>2</sub>-(484)

B.P. 326°

M.P. 29°

*See 3:0180. Division A: Solids.*

## — HEXACHLOROBENZENE



Beil. V - 205

V<sub>1</sub>-(113)V<sub>2</sub>-(157)

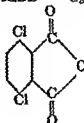
B.P. 326°

M.P. 220°

*See 3:4333. Division A: Solids.*

—— 3,6-DICHLOROPHTHALIC ANHYDRIDE  $C_8H_2O_3Cl_2$

Beil. XVII - 483  
XVII<sub>1</sub>-(254)



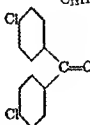
B.P. 339°

M.P. 194°

See 3:4860. *Division A: Solids.*

—— 4,4'-DICHLOROBENZOPHENONE  $C_{13}H_8OCl_2$

Beil. VII - 420  
VII<sub>1</sub>-(228)



B.P. 353° at 767 mm.

M.P. 145°

See 3:4270. *Division A: Solids.*

—— OCTACHLORONAPHTHALENE  $C_{10}Cl_8$

Beil. V - 547  
V<sub>1</sub>—  
V<sub>2</sub>-(446)



B.P. 440-442°

M.P. 203°

See 3:4893. *Division A: Solids.*

## CHAPTER XVI

### DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

#### Section 2. $D_4^{20}$ less than 1.1500

(3:7000-3:7499)

3:7000	CHLOROACETYLENE (Chloroethyne)	$\text{HC}\equiv\text{C}-\text{Cl}$	$\text{C}_2\text{HCl}$	Beil. I - 244 I <sub>1</sub> -(106) I <sub>2</sub> -(221)
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B.P.  $-29.6^\circ$  (1)  
 $-32$  to  $-30^\circ$  (2)

[See also dichloroacetylene (3:5010).]

$\bar{\text{C}}$  is a gas with extremely nauseating odor reminiscent both of yellow phosphorus and of carbylamines; its inhalation even in traces produces very unpleasant symptoms. It is also treacherously explosive and may detonate during manipulation (2). —  $\bar{\text{C}}$  ignites spontaneously in air (6) (3).

[For prepn. of  $\bar{\text{C}}$  from *cis*-1,2-dichloroethylene (3:5042) via treatment in dil. alc. with aq. alk.  $\text{Hg}(\text{CN})_2$  to yield  $\text{Hg}(\text{C}\equiv\text{CCl})_2$  (see below) which is then warmed (under  $\text{N}_2$ ) with alk.  $\text{NaCN}$  soln. see (1) (2) (3) (4)] cf. (7).

[For formn. of  $\bar{\text{C}}$  during reaction of 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) with solid  $\text{KOH}$  see (5); from 1,2-dichloroethylene with alc.  $\text{KOH}$  see (3) (4); from  $\beta,\beta$ -dichloroacrylic acid (3:1575) with  $\text{Ba}(\text{OH})_2$  see (6).]

$\bar{\text{C}}$  with  $\text{NH}_4\text{OH}/\text{CuCl}$  gives (3) (6) an explosive ppt. —  $\bar{\text{C}}$  with  $\text{NH}_4\text{OH}/\text{AgNO}_3$  gives (2) (3) a ppt. of silver salt, which is extremely explosive, detonating with great violence not only in dry state but also when moist and even under water, quantities as small as 0.1 g. causing considerable damage (2).

$\bar{\text{C}}$  with aq. alk.  $\text{Hg}(\text{CN})_2$  yields (3) (4) (1) (2) a mercury salt,  $\text{Hg}(\text{C}\equiv\text{CCl})_2$ , cryst. from  $\text{CHCl}_3$  (1) (2) (3) (4), m.p.  $185^\circ$  (1) (4),  $186^\circ$  (2); explodes at  $195^\circ$  with flame and deposition of soot (3) (4). [This prod. with alk.  $\text{KCN}$  evolves  $\bar{\text{C}}$  (use in prepn. of  $\bar{\text{C}}$  as above).]

$\bar{\text{C}}$  with  $\text{Br}_2/\text{aq.}$  yields (6) 1-chloro-1,1,2,2-tetrabromoethane [Beil. I-95], m.p.  $33-34^\circ$  (6). [For other reactns. see (2) (7); for study of oxidation of  $\bar{\text{C}}$  see (1).]

3:7000 (1) Bashford, Emelius, Briscoe, *J. Chem. Soc.* 1938, 1358-1364. (2) Ingold, *J. Chem. Soc.* 123, 1535-1536 (1924). (3) Hofmann, Kirmreuther, *Ber.* 42, 4232-4238 (1909). (4) Hofmann, Kirmreuther, *Ber.* 41, 314-317 (1908). (5) Saxby, *J. Soc. Chem. Ind.* 33, 450-452 (1916). (6) Wallach, *Ann.* 203, 87-94 (1880). (7) Ort, Dittus, Weissenburger, *Ber.* 76, 57-58 (1943).

3:7005	CHLOROMETHANE (Methyl chloride)	$\text{CH}_3\text{Cl}$	$\text{CH}_3\text{Cl}$	Beil. I - 59 I <sub>1</sub> -( 8) I <sub>2</sub> -(11)
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B.P.  $-24.22^\circ$  at 760 mm. (1)  
 $-23.7^\circ$  at 760 mm. (3) (4)

M.P.  $-97.72^\circ$  (1)  
 $-96.65^\circ$  (2)

$n_D^{25} = 1.3830$  (5)





3:7015 ETHYL CHLORIDE  
(Chloroethane)



Boil. 1 - 82  
I<sub>1</sub>-(23)  
I<sub>2</sub>-(50)

B.P.		F.P.	
+13.1°	at 760 mm. (1) (2)	-142.5° (15)	$[D_4^{15} = 0.90280 \text{ (11)}]$
12.6°	(3)	-141.6° (16)	$n_D^{20} = 1.3790 \text{ (10)}$
[12.5-12.6° at 725 mm. (4)]		-140° (17)	$D_{12}^{12} = 0.8510 \text{ (19)}$
12.52°	(5)	-139.4° (18)	$n_D^{20} = 1.3913 \text{ (2)}$
12.50°	(6)	-138.7° (1)	$D_4^{25} = 0.9176 \text{ (12)}$
12.5°	(7) (8) (9)	-136.4° (11)	$n_D^{30} = 1.4085 \text{ (2)}$
12.4°	(10)		$D_0^{20} = 0.92138 \text{ (20)}$
12.3°	at 760 mm. (11)		
12.18°	at 760 mm. (12)		
12-12.5°	(13) (14)		

Colorless mobile liq. with pungent ethereal odor and sweetish taste. —  $\bar{C}$  is inflammable (see also below) and burns with smoky green-edged flame producing fumes of HCl.

### SELECTED PHYSICAL PROPERTIES

Vapor pressure. [For vapor-press. data over various temp. ranges, e.g., from -30 to +40° (5), -30° to 100° (21), 12-187° (4) (22), see indic. refs.]

Solubility relations.  $\bar{C}$  is very spar. sol. aq., e.g., 100 g. aq. at 0° dis. 0.447 g.  $\bar{C}$  (23), 0.570 wt. % (24), although even this is somewhat more than its homologs (24).

$\bar{C}$  is miscible with EtOH although forced out of soln. by addn. of aq. (25); for use of mixt. of EtOH (50-80%) + aq. (50-20%) as selective solv. for  $\bar{C}$  in sepn. from butane see (26). —  $\bar{C}$  is also miscible with ether. — [For study of rate of volatilization of  $\bar{C}$  from solns. in ether or oils see (32).]

[For soly. of  $\bar{C}$  in  $\text{CCl}_4$  (3:5100) or in ethylene dichloride (3:5130) at -10° and 20° and at 100-760 mm. press. see (27); for soly. of  $\bar{C}$  in various high-boilg. ethers and esters of interest to refrigeration industry see (28) (29); for solubility, density, b.p., vapor/liq. equil., etc., of system  $\bar{C}$  + kerosene see (30); for sepn. of  $\bar{C}$  from butane by azeotropic distn. with  $\text{SO}_2$  see (31).]

[For soly. in  $\bar{C}$  of anhydrous  $\text{FeCl}_3$  (33) (34) or anhydrous  $\text{AlCl}_3$  (35) (36) see indic. refs.]

Adsorption of  $\bar{C}$ . [For studies on adsorption of vapors of  $\bar{C}$  by activated carbon at -15° (37), 0° (37) (38), 20° (37), 25° (39), or 50° (40) see indic. refs. and also (41); for sepn. of  $\bar{C}$  from ethylene + HCl gas by adsorption on carbon see (42). — For adsorption of vapors of  $\bar{C}$  by dehydrated chabazite see (43).]

Inflammability of  $\bar{C}$  or its mixtures.  $\bar{C}$  is readily inflammable; in mixts. with air explosive range conts. 4.00-14.18 vol. %  $\bar{C}$  with minimum ignition temp. 517°C. (44) cf. (47) (48); in mixts. with  $\text{O}_2$  explosive range conts. 4.05-67.2 vol. %  $\bar{C}$  (44) (45) with min. ignition temp. 463°C.; in mixts. with  $\text{N}_2\text{O}$  explosive range conts. 2.1-32.8 vol. %  $\bar{C}$  (45) cf. (46); for study of explosion range of  $\bar{C}$  +  $\text{C}_2\text{Cl}_2\text{F}_2$  ("Freon") + air or  $\bar{C}$  + butane + air see (49). — See also below under use of  $\bar{C}$  as anesthetic.

Other miscellaneous physical props. [For study of thermal conductivity of  $\bar{C}$  see (50).]

Binary systems contg.  $\bar{C}$ . [For f.p./compu. data and diagram of system  $\bar{C}$  + methylene (di)chloride (3:5020), eutectic, f.p. -149.7°, contg. 68.3 wt. %  $\bar{C}$ , see (18); for f.p./compu. data and diag. of system  $\bar{C}$  + EtBr (note no eutectic is formed) see (18); for system  $\bar{C}$  + solid  $\text{CO}_2$  see (5) ]

TOXICITY AND PHYSIOLOGICAL ACTION OF  $\bar{C}$ 

Full treatment of this topic is beyond the scope of this work; however, for lead references on its pharmacology (51), toxicity (52) (53) (54) (55), or anthelmintic props. (56) see indic. refs. — For use as narcotic and anesthetic see below.

USES OF  $\bar{C}$ 

Use for anesthesia and narcosis. [For general reviews on use of  $\bar{C}$  as anesthetic see (57) (58) (59) (60); for use of  $\bar{C}$  as dental anesthetic see (61) (62) (63); for short narcosis see (64) (65). — For data on mortality from use of  $\bar{C}$  as anesthetic see (66). — For studies of explosion hazards with  $\bar{C}$  or  $\bar{C}$  + ether (67) especially in presence of X-ray apparatus (68) see indic. refs. (see also above under inflammability of  $\bar{C}$ ).]

Use as a refrigerant.  $\bar{C}$  either alone or mixed with other cpds. is often used in refrigerating systems: e.g., for general survey of this aspect see (21); for examples of patents on use in refrigerating systems of  $\bar{C}$  (70), of  $\bar{C}$  (96%) + MeCl (4%) (3:7005) (71), of  $\bar{C}$  (25%) + methylene (di)chloride (3:5020) (75%) (72), of  $\bar{C}$  (40%) + EtBr (60%) (72), of  $\bar{C}$  + an alc. + a hydrocarbon lubricant (74) see indic. refs. — For study of use of  $\bar{C}$  with other suitable liq. in low-temp. cryostats see (18).

Use as solvent for extraction of oils. For use of  $\bar{C}$  as extremely volatile solvent for extraction of oils, fats, resins, perfumes, etc., see (75) (76) (77).

Miscellaneous uses of  $\bar{C}$ .  $\bar{C}$  is now an important raw material in the prepn. of tetraethyllead for use as an anti-knock agent in gasoline; for further details see below under chem. behavior of  $\bar{C}$  toward metals.

[For use of  $\bar{C}$  in purification of metallic mercury see (78).]

Because of its inertness toward ozone, its availability, and its low b.p.,  $\bar{C}$  is often used as solvent for ozonolysis.

DETERMINATION OF  $\bar{C}$ 

For detn. of  $\bar{C}$  by pyrolytic dissociation at 900° into ethylene and HCl, followed by detn. of chloride ion with stand. AgNO<sub>3</sub> (42) (80) cf. (81) or by combustion with O<sub>2</sub> in an explosion pipet to yield H<sub>2</sub>O, CO<sub>2</sub> + HCl (47), see indic. refs. — For detn. of  $\bar{C}$  by hydrolysis with excess std. N/2 alc. KOH in a.t. at 120° for 15 min. and back titration with N/2 HCl see (79).

For detn. of  $\bar{C}$  in CHCl<sub>3</sub> (3:5050) see (82); for detection of  $\bar{C}$  in perfumes see (83).

For further aspects of identification of  $\bar{C}$  see below under  $\bar{C}$ .

PREPARATION OF  $\bar{C}$ 

$\bar{C}$  can be prepared from various sources and by many methods (see simplification below); however, for quick laboratory methods the most convenient are those from EtOH by hgt. with AlCl<sub>3</sub> (1 mole) at 150° (97.6% yield (13)) and from diethyl sulfate with aq. CaCl<sub>2</sub> (63% yield (84)).

From ethyl alcohol (1:0130).

With hydrogen chloride or hydrochloric acid. [For prepn. of  $\bar{C}$  from EtOH by reactn. with HCl in absence of cat. under reflux (85) (86) or at 125° and 16 atm. (87), or 140° and 24 atm. (88), see indic. refs.; for use of EtOH + liq. HCl see (89).]

For prepn. of  $\bar{C}$  from EtOH with conc. HCl in pres. of ZnCl<sub>2</sub> (60% yield (7) (91)) see articles represented by (90) (7) (91) (92) (93) [for patents (often including also other metal salt cat. such as BiCl<sub>3</sub>, etc.) see (94)–(102), incl.].

[For prepn. of  $\bar{C}$  from EtOH + HCl in pres. of H<sub>3</sub>PO<sub>4</sub> (103) (104) (105) or H<sub>2</sub>SO<sub>4</sub> (106) or EtHSO<sub>4</sub> (107) see indic. refs.]

*By use of metal salts* For prepn. of  $\bar{C}$  from EtOH by use of  $AlCl_3$  at  $150^\circ$  (97.6% yield (13)) or of aq.  $FeCl_3$  at  $80^\circ$  (108), or by reflux with subl.  $FeCl_3$  for  $1\frac{1}{2}$  hrs. (86% yield (112)), see iodic. refs.

*By use of inorganic acid chlorides.* For prepn. of  $\bar{C}$  from EtOH by use of  $PCl_3$  (43% yield (109)),  $PCl_3 + ZnCl_2$  (62% yield (91)),  $PCl_5 + ZnCl_2$  (70% yield (91)),  $SOCl_2 + pyridine$  (75% yield (91)), or  $SO_2Cl_2 + pyridine$  (110) see indic. refs.

*By use of organic acid chlorides.* [For prepn. of  $\bar{C}$  from EtOH with benzotrichloride (3:6540) +  $FeCl_3$  see (111)]

From diethyl ether (1:6110).

*By cleavage with HCl + a catalyst.* [For prepn. of  $\bar{C}$  from diethyl ether with  $HCl + ZnCl_2$  (113) at  $80-280^\circ$  under press. (114) or at  $300-370^\circ$  under press. (115), or with  $HCl + AlCl_3/NaCl/FeCl_3$  at  $200-325^\circ$  (116), or with  $HCl +$  a nitrogen heterocycle (117) see iodic. refs.]

*By cleavage with acid chlorides + a catalyst.* [For prepn. of  $\bar{C}$  from diethyl ether with  $SOCl_2$  or  $S_2Cl_2$  in pres. of  $SnCl_4$  or  $TiCl_4$  (118), or with  $SOCl_2 + ZnCl_2$  (119); or with benzoyl chloride (3:6240) in pres. of  $Zn$  (120) cf. (121),  $ZnCl_2$  at  $150^\circ$  (78% yield (122)) cf. (123) (124),  $MeZnI$  (125) or  $AlCl_3$  (126), or with phthalyl (di)chloride (3:6900) in pres. of  $ZnCl_2$  at  $170^\circ$  (80% yield (122)); or with acetyl chloride (3:7065) in pres. of  $ZnCl_2$  (127) or  $AlCl_3$  (126) see indic. refs.]

[For formn. of  $\bar{C}$  from diethyl ether +  $CHCl_3$  (3.5050) + cat. at  $200^\circ$  and 25 atm. see (128)]

*From various ethyl esters of inorganic and organic acids.* [For prepn. of  $\bar{C}$  from diethyl sulfate with aq.  $CaCl_2$  as lab. method (63% yield (84)) or as manufacturing process (129); from diethyl sulfate with conc.  $HCl$  at  $140^\circ$  and 24 atm. (130), from ethyl chlorosulfonate with fuming  $HCl$  at  $100^\circ$  (91% yield (131)) (132) cf. (189), pyridine (133), or di-*n*-butylamine at  $100^\circ$  (53% yield (134)) see indic. refs.]

[For prepn. of  $\bar{C}$  from ethyl formate (1:3000) with  $AlCl_3$  (1 mole) at  $110^\circ$  (82% yield (135)); from ethyl chloroformate (3:7295) on litg. at  $250^\circ$  (for study of this reaction see (136) (137)), with dimethylaniline at  $150^\circ$  (138), with pyridine (139), with quinoline at  $100^\circ$  (139) or even  $59^\circ$  (140) (141), or with  $AlCl_3$  at room temp. (142), or with  $EtHSO_4$  (143) see indic. refs.]

[For prepn. of  $\bar{C}$  from ethyl acetate (1:3015) with subl.  $FeCl_3$  on  $1\frac{1}{2}$  hrs. reflux (73% yield (112)), or with  $SiCl_4$  (144), from ethyl benzoate (1:3721) with subl.  $FeCl_3$  on  $1\frac{1}{2}$  hrs. reflux (74% yield (112)); or from diethyl phthalate (1:4331) with phthalyl (di)chloride (3:6900) + trace  $ZnCl_2$  at  $130^\circ$  (145) see indic. refs.]

From vinyl chloride (3:7010). [For prepn. of  $\bar{C}$  from vinyl chloride by cat. hydrogenation at elev. temp. and press. see (146)]

From ethane. [For prepn. of  $\bar{C}$  from ethane with  $Cl_2$  above  $200^\circ$  in pres. of ethylene or  $PbEt_4$  as cat. (yields 67.8-71.4% (147)) (148) see indic. refs. — For examples of other patents on prepn. of  $\bar{C}$  from ethane with  $Cl_2$  in pres. of various cat. (149) (150) (151) (152) (153) see indic. refs.]

From ethylene. The preparation of  $\bar{C}$  from ethylene by catalytic addn. of hydrogen chloride has been extensively studied both in the scientific and in technical literature. At very low temperatures, the catalyzed reaction is quantitative, but as the temperature is increased the reverse reaction (dissociation of  $\bar{C}$  into ethylene and  $HCl$ ) is favored.

[For studies on the prepn. of  $\bar{C}$  from ethylene with  $HCl$  in pres. of  $AlCl_3$  or  $BiCl_3$  at  $-78^\circ$  (100% yield (3) (155)), or as high as  $-12^\circ$  (95% yield (151) (155)) or  $130^\circ$  (37% yield (42)), see indic. refs.; for studies on equilibrium at  $114^\circ$  and  $124^\circ$  (156), at  $170^\circ$ ,  $200^\circ$ , and  $230^\circ$  (157) or for calcul. of entropy of system (158) see indic. refs.; for study of various cat. see (159)]



[The patent literature on prepn. of  $\bar{C}$  from ethylene + HCl is extensive and overlapping, but illustrative examples may be cited. For patents involving use of  $AlCl_3$  (160) (161) under pressure (162) (163) (164) (165) in the pres. of a solvent (often  $\bar{C}$  itself) (162) (166) (167) (168) (190) see indic. refs. — For use of ethylene + mixt. of HCl (90%) +  $Cl_2$  (10%) +  $AlCl_3$  (169) (170) or for prepn. (171) or revivification (172) of  $AlCl_3$  cat. see indic. refs.]

[For patents on prepn. of  $\bar{C}$  from  $C_2H_4$  + HCl with various cat., e.g., with  $BiCl_3$  (173) (174) (175), with anhydrous  $EtHSO_4$  (176), with  $SnCl_4$  on activated carbon at  $150^\circ$  (177), with bauxite cat. (178), with iron oxide cat. at  $50^\circ$  and ord. or increased press. (179), with  $BaCl_2$  at  $250^\circ$  (180), with  $FeCl_3$  in  $\bar{C}$  or  $AlCl_3$  in nitrobenzene (181), with  $ZnCl_2$  on activated carbon, silica gel, etc., (182) (183), with various surface agts. (184) (185), with  $SO_2$  (186), with 00%  $H_2SO_4$  + NaCl (188), or in liq. ethyl chlorosulfonate +  $BiCl_3$  (189) see indic. refs.]

[For purification of  $\bar{C}$  obtd. from techn. gases by HCl method see (187).]

From miscellaneous sources. [For formn. of  $\bar{C}$  from  $EtBr$  with  $CHCl_3$  (3:5050) in pres. of  $AlCl_3$  at  $50^\circ$  (191), from  $EtMgBr$  during reaction with  $S_2Cl_2$  (102) or with 1,2-dichloroethylene (3:5030) (193), from  $EtI$  with  $Hg_2Cl_2$  in s.t. at  $140^\circ$  (12), from ethyl  $\alpha,\beta$ -dichlorovinyl ether (3:5540) with  $Cl_2$  at ord. temp. followed by warming, or stdg. in absence of aq. (194), or from dichloroacetaldehyde diethylacetal (3:6110) with  $ZnEt_2$  (195) see indic. refs.]

[For formn. of  $\bar{C}$  from succinic acid (1:0530) with aq.  $FeCl_3$  in sunlight (196) or from  $MeCl$  (3:7005) + aq. by disproportionation over cat. at  $200$ – $275^\circ$  (107) see indic. refs.]

## CHEMICAL BEHAVIOR OF $\bar{C}$

### Pyrolysis of $\bar{C}$

$\bar{C}$  passed through plain tube at  $410^\circ$  is largely unchanged, but  $\bar{C}$  passed at  $550^\circ$  through tube contg. pumice (108) cf. (42) or other cat. (100) dissociates completely into ethylene + HCl (see in detn. of  $\bar{C}$  (42)).

### BEHAVIOR OF $\bar{C}$ WITH INORGANIC REACTANTS

Chlorination. [ $\bar{C}$  with liq.  $Cl_2$  (1 mole) in u.v. light and cooling yields (200) mainly 1,1-dichloroethane (3:5035) accompanied by some 1,2-dichloroethane (3:5130) and higher chlorination prods.; the two dichloroethanes are also obtd. from  $\bar{C}$  with  $Cl_2$  + aq. (201). — For very imp. study of behavior of  $\bar{C}$  with  $Cl_2$  at  $202$ – $380^\circ$  see (202) (147).]

[ $\bar{C}$  with  $SbCl_5$  in s.t. at  $100^\circ$  (203) or  $\bar{C}$  with  $NCl_3$  (204) yields 1,2-dichloroethane (ethylene dichloride) (3:5130).]

Bromination. [For behavior of  $\bar{C}$  with  $Br_2$  see (207) (208).]

Fluorination. [ $\bar{C}$  at  $900^\circ$  with  $F_2$  in pres. of Cu yields (205)  $CF_4$ ,  $CF_3Cl$ ,  $CF_3CF_2Cl$ ,  $CHF_2CH_2Cl$ ,  $CF_2=CCl_2$ , and other prods.]

Hydrogenation. [For behavior of  $\bar{C}$  with atomic hydrogen see (206).]

Hydrolysis. [ $\bar{C}$  over suitable partially dehydrated  $Al(OH)_3$  at room temp. (209), or  $\bar{C}$  + aq. vapor over cat. at  $300$ – $500^\circ$  at ord. press. (210) (211) (212), or  $\bar{C}$  with aq. NaOH above  $150^\circ$  under press. (213), or  $\bar{C}$  with alc. NaOH (214), alc.  $Na_2CO_3$ , MgO, or CaO (215) is saponified yielding EtOH (1:0130). — The reaction of  $\bar{C}$  with EtOH/KOH is bimolecular (216); furthermore during hydrol. of  $\bar{C}$  with alk. some diethyl ether is always formed cf. (213) (214) and the reaction may be adapted to its prepn. (217).]

Amination. [ $\bar{C}$  with alc.  $NH_3$  in s.t. at  $100^\circ$  (218) or  $\bar{C}$  with liq.  $NH_3$  at  $220^\circ$  and 220 atm. press. (219) gives salts of ethylamine, diethylamine, triethylamine, and other prods. —

$\bar{C}$  with  $\text{NaNH}_2$  in liq.  $\text{NH}_3$  at  $0^\circ$  and 20 atm. gives ethylamine (30% yield (220)) and ethylene.]

Behavior of  $\bar{C}$  with inorganic acids. [ $\bar{C}$  passed through boilg.  $\text{H}_2\text{SO}_4$  gives  $\text{C}_2\text{H}_4 + \text{SO}_2 + \text{HCl}$ ;  $\bar{C}$  is absorbed by  $\text{SO}_3$  giving a liq. which probably comprises a mixture of ethyl chlorosulfonate,  $\beta$ -chloroethanesulfonic acid, and  $\beta$ -hydroxyethanesulfonyl chloride (221).]

Behavior of  $\bar{C}$  with inorganic salts. [For study of rate of reaction of  $\bar{C}$  with  $\text{KI}$  in acetone at  $50^\circ$  and  $60^\circ$  see (222). —  $\bar{C}$  with  $\text{AlBr}_3$  under suitable cond. yields (223) ethyl bromide.]

Behavior of  $\bar{C}$  with metals. With sodium. The most important reaction of  $\bar{C}$  with metals is that involved in the manufacture of tetraethyllead for use as an anti-knock agent in motor fuels. Tetraethyllead is prepared for  $\bar{C}$  either by direct reaction with  $\text{Na/Pb}$  alloys, or by reaction with  $\text{Mg}$  and subsequent conversion of the  $\text{EtMgCl}$  by means of  $\text{PbCl}_2$ . For a general survey (without references) on the manufacture of tetraethyllead see (224).

For patents involving the prepn. of  $\text{Et}_4\text{Pb}$  from  $\bar{C}$  by reactn with  $\text{Na/Ph}$  alloys under various circumstances see (225)–(244) incl.; for patents involving the use of  $\text{EtMgCl}$  see (245)–(248) incl.

[For behavior of  $\bar{C}$  with  $\text{Na}$  in lgr. followed by  $\text{CO}_2$  (249) or with amyl-sodium or octyl-sodium (250) see indic. refs. —  $\bar{C}$  with  $\text{K/Na}$  alloy in xylene gives (251) ethane (32%) and ethylene (5.5%). —  $\bar{C}$  with  $\text{Ti/Na}$  yields (252)  $\text{TiEt}_3$ .]

With magnesium. [ $\bar{C}$  with  $\text{Mg}$  in a.t. at  $260^\circ$  for 4 hrs gives (253) gas (consisting of 45% butane + 20% olefins + 22%  $\text{H}_2$ ) and a white solid which with aq. gives a gas contg. 86%  $\text{H}_2$  + 13% ethane]

$\bar{C}$  with  $\text{Mg}$  in dry ether in absence of air and in pres. of trace of  $\text{I}_2$  gives (99.7% yield in 4 hrs. (254))  $\text{EtMgCl}$ ; this reagt. is actually an equil. mixt. contg. 25%  $\text{EtMgCl}$  + 42.5%  $\text{MgEt}_2$  + 42.5%  $\text{MgCl}_2$  (255). — For study of competitive reaction with  $\text{Mg}$  in ether of an equimolar mixt. of  $\bar{C}$  +  $\text{EtI}$  yielding 27%  $\text{EtMgCl}$  + 73%  $\text{EtMgI}$  see (256). — [For reactn. of  $\text{EtMgCl}$  with  $\text{NH}_4\text{Cl}$  or triethylamine. $\cdot\text{HCl}$  (254), with  $\text{NH}_2\text{Cl}$  (257), or with  $\text{NCl}_3$  (258) see indic. refs.; for study of electrolysis of  $\text{EtMgCl}$  in ether see (259). — For reactn. of  $\text{EtMgCl}$  with  $\text{PbCl}_2$  yielding  $\text{PbEt}_4$  see (245)–(248) incl.; with  $\text{C}_6\text{H}_5\text{NCO}$  yielding propionanilide see below under  $\text{C}_6\text{H}_5\text{NCO}$ .]

#### BEHAVIOR OF $\bar{C}$ WITH ORGANIC REAGENTS

[ $\bar{C}$  with  $\text{C}_6\text{H}_6$  +  $\text{Al/Hg}$  gives (76% yield (260)) ethylbenzene (1:7410);  $\bar{C}$  + hexane +  $\text{AlCl}_3$  gives (261) octane.]

[ $\bar{C}$  with  $\text{CO}$  +  $\text{AlCl}_3$  at  $40$ – $50^\circ$  and 120 atm. followed by treatment with  $\text{H}_2\text{O}$  gives (43% yield (262)) (263) propionic acid (1:1025).]

[ $\bar{C}$  with ethylene oxide (1:6105) +  $\text{AlCl}_3$  gives (264) a mixt. contg. 4-chlorobutanol-1 (3:9170) + ethylene chlorohydrin (3:5552).]

[ $\bar{C}$  may be used for the ethylation of  $\text{OH}$  groups or  $\text{NH}_2$  groups: e.g., for reaction of  $\bar{C}$  with sodium phenolate yielding (265) ethyl phenyl ether (1:7485) or for use of  $\bar{C}$  in ethylation of cellulose (266) (267) see indic. refs.; for use of  $\bar{C}$  in ethylation of metanilic acid (268) (214) (215), *o*-toluidine (269), or *m*-aminophenol (268) see indic. refs.]

[For condens. of  $\bar{C}$  with hexamethylenetetramine see (270).]

[ $\bar{C}$  (2 moles) with ethylene (di)bromide (1 mole) + 3%  $\text{AlCl}_3$  in steel bomb at  $25^\circ$  for 14 days undergoes a redistribution reactn. yielding (271) a mixt. consisting of 5 cpds., viz.,  $\bar{C}$  (35 mole %) +  $\text{EtBr}$  (30 mole %) + ethylene chlorobromide (17 mole %) + ethylene (di)bromide (11 mole %) + ethylene dichloride (3.5130) (7 mole %).]

[ $\bar{C}$  (1 mole) with quinoline (1 mole) in a.t. in direct sunlight reacts only very slowly (incomplete in 1 year) but grad. separates ethylquinolium chloride, cryst. from abs.  $\text{EtOH}$  by addn. of dry ether, m.p.  $122^\circ$  (290).]

- ③ Propionanilide: m.p. 104.0–104.5° u.c. (272). (See also under propionic acid (1:1025).) [From  $\bar{C}$  by conversion to EtMgCl (see above) and reactn. in dry ether with phenyl isocyanate (272).]
- Propion-*p*-toluidide: m.p. 123°. [Presumably obtainable (272) from  $\bar{C}$  via conversion to EtMgCl (see above) and reaction in dry ether with *p*-tolyl isocyanate.]
- Propion- $\alpha$ -naphthalide: m.p. 126° u.c. (273). [Presumably obtainable (272) from  $\bar{C}$  via conversion to EtMgCl (see above) and reaction in dry ether with  $\alpha$ -naphthyl isocyanate; the analogous process for EtBr has been reported (273).]
- Ethyl mercuric chloride: m.p. 193.5° cor. (274), 192.5° (275), 192° (276). [Prepd. indirectly (276); but should be preparable from EtMgCl with HgCl<sub>2</sub> since corresp. EtHgBr has been reported (276) from EtMgBr + HgBr<sub>2</sub>. — Note that m.p. of EtHgCl is almost identical with that (193.5°) of EtHgBr cf. (276).]
- *S*-(Ethyl)isothiourea picrate: m.p. 188° (277). [Not reported from  $\bar{C}$ , but readily obtd. from EtBr or EtI (277) (278) (1 g.) with thiourea (1 g.) in alc. (10 ml.) on refluxing for 2 hrs., then adding PkOH (1 g.), htg. until clear soln. results, then cooling (277). — Note that the m.p. of this prod. is very close to those of *S*-(*sec*-butyl)isothiourea picrate, m.p. 190° (278), and *S*-benzylisothiourea picrate, m.p. 188° (277).]
- *N*-Ethylphthalimide: [Beil. XXI-461, XXI-(363)], ndls. from alc., m.p. 79° (279), 78° (280). [Prepd. indirectly (280), also from EtI with potassium phthalimide in s.t. at 150° (279).]
- *N*-Ethyl-3-nitrophthalimide: pl. from CS<sub>2</sub>, m.p. 105–106° (281) (282); for photographs of crystals see (282). [Not reported from  $\bar{C}$  itself, but obtd. from EtBr with K phthalimide on protracted reflux. (281).]
- *N*-Ethyltetrachlorophthalimide: pl. from CHCl<sub>3</sub> on pouring into 2 vols. EtOH, m.p. 192–193° (283). [Not reported from  $\bar{C}$  but obtd. from EtBr or EtI with K tetrachlorophthalimide in s.t. at 200° for 6 hrs. (283).]
- *N*-Ethylsaccharin: cryst. from dil. alc., m.p. 94° (284). [This prod. cannot be obtd. from  $\bar{C}$  itself (284) but is obtd. from either EtBr or EtI with sodium saccharin in aq. butylcarbitol (1:6517) contg. KI on refluxing for 30 min. (284).]
- *N*-Ethyl-*N*-(*p*-bromobenzenesulfonyl)-*p*-aniside: m.p. 113.5° u.c. (285). [Not reported from  $\bar{C}$  but obtained from EtBr with *N*-(*p*-bromobenzenesulfonyl)-*p*-aniside (285).]
- *p*-Ethoxybenzoic acid: m.p. 195° (286) cf. (287).
- Ethyl 2,4,6-triiodophenyl ether: m.p. 83.5° cor. (288).
- Ethyl  $\alpha$ -naphthyl ether: oil, b.p. 280.5° cor., f.p. below -10° (289). (Corresp. picrate, m.p. 118.5–119.5° cor.; Neut. Eq. 401 (289).)
- Ethyl  $\beta$ -naphthyl ether: m.p. 35.5–36.0° cor., b.p. 282° cor. (289). (Corresp. picrate, m.p. 101.0–101.5° cor., Neut. Eq. 401 (289).)

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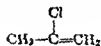
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### 3:7020 2-CHLOROPROPENE-1

(Isopropenyl chloride  
 $\alpha$ -methylvinyl chloride)



$\text{C}_3\text{H}_5\text{Cl}$

Beil. I-198

I<sub>1</sub>-(82)

I<sub>2</sub>-(169)

B.P.

22.65° at 760 mm. (1)

22.6° at 760 mm. (2)

22.5-23.5° at 760 mm. (3)

21.7-21.8° at 743 mm. (4)

F.P.

-138.6° (2)

-137.4° (1)

$D_4^{20} = 0.918$  (5)

$n_D^{20} = 1.3949$  (4)

[For prepn of  $\bar{\text{C}}$  (45%) together with 2,2-dichloropropane, b.n. 70° (3.7-4.1), from acetone (1:5400) +  $\text{PCl}_3$  see {61} 474 (5).  
KOH (3) or  $\text{KOC}_2\text{H}_5$  (4) (1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11) (12) (13) (14) (15) (16) (17) (18) (19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30) (31) (32) (33) (34) (35) (36) (37) (38) (39) (40) (41) (42) (43) (44) (45) (46) (47) (48) (49) (50) (51) (52) (53) (54) (55) (56) (57) (58) (59) (60) (61) (62) (63) (64) (65) (66) (67) (68) (69) (70) (71) (72) (73) (74) (75) (76) (77) (78) (79) (80) (81) (82) (83) (84) (85) (86) (87) (88) (89) (90) (91) (92) (93) (94) (95) (96) (97) (98) (99) (100) (101) (102) (103) (104) (105) (106) (107) (108) (109) (110) (111) (112) (113) (114) (115) (116) (117) (118) (119) (120) (121) (122) (123) (124) (125) (126) (127) (128) (129) (130) (131) (132) (133) (134) (135) (136) (137) (138) (139) (140) (141) (142) (143) (144) (145) (146) (147) (148) (149) (150) (151) (152) (153) (154) (155) (156) (157) (158) (159) (160) (161) (162) (163) (164) (165) (166) (167) (168) (169) (170) (171) (172) (173) (174) (175) (176) (177) 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Weidenbaur  
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3:7022 ETHYL HYPOCHLORITE  $\text{CH}_3\text{CH}_2\text{OCl}$   $\text{C}_2\text{H}_5\text{OCl}$  Beil. I- 324  
I<sub>1</sub>-(164)  
I<sub>2</sub>-(325)

B.P. 36° at 758 mm. (1)

$D_4^{20} = 1.013$  (1)

36° at 752 mm. (2)

[See also *ter-butyl hypochlorite* (3:7165).]

Colorless oil (rapidly turning yellow in light) with odor like hypochlorous acid. —  $\bar{\text{C}}$  explodes on superhtg. its vapor or even in cold upon addn. of Cu powder or in bright sunlight —  $\bar{\text{C}}$  gradually decomposes on stdg. in diffuse light with formn. of ethyl acetate and other prods. (3) (4) (10). [For study of stability of  $\bar{\text{C}}$  in aq. or in  $\text{CCl}_4$  soln. see (4).] — Sol. ether,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ ; for distrib. of  $\bar{\text{C}}$  between aq. and  $\text{CCl}_4$  see (4).

[For prepn. of  $\bar{\text{C}}$  from EtOH (1:6130) with  $\text{Cl}_2$  in cold aq. alk. (2) (5) (1) (6) (7) (8) (9) or alk. earth (9) or with aq. HOCl in pres. of  $\text{CCl}_4$  (4) see indic. refs.; for formn. of  $\bar{\text{C}}$  from EtOH (1:6130) with  $\text{Cl}_2$  at  $-18^\circ$  (8) or with dry  $\text{Ca}(\text{OCl})_2$  (15) or aq. HOCl (15) (16) see indic. refs.]

$\bar{\text{C}}$  is able according to prevailing circumstances to act as an oxidizing agent, chlorinating agent, or for addn. to unsaturated linkages: furthermore since in aq.  $\bar{\text{C}}$  is extensively hydrolyzed (69% in sat. aq. soln. (4)) it may serve as source of HOCl; examples of these reactions are given below.

$\bar{\text{C}}$  with inorganic reactants.  $\bar{\text{C}}$  with KI + AcOH liberates  $\text{I}_2$  quant. according to the equation  $\text{C}_2\text{H}_5\text{OCl} + 2\text{HI} \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{HCl} + \text{I}_2$  (use in quant. detn. of  $\bar{\text{C}}$  (2) (4) (7));  $\bar{\text{C}}$  with dil. alk.  $\text{Na}_3\text{AsO}_3$  gives (11) (12)  $\text{EtCl}$  (3:7015) +  $\text{Na}_3\text{AsO}_4$ ;  $\bar{\text{C}}$  in dil. alk. KSH/KCN mixt. gives (12)  $\text{KSCN} + \text{KCl} + \text{EtOH}$ .

[ $\bar{\text{C}}$  adds to dry  $\text{SO}_2$  yielding (5) ethyl chlorosulfonate [Beil. I-327, I<sub>2</sub>-(327)], b.p. 151-154° dec.,  $n_D^{20} = 1.4174$ ]

[ $\bar{\text{C}}$  (1 mole) with KCN (2 moles) in 7 pts. aq. at  $-5^\circ$  gives (30% yield (13)) ethyl cyaniminoformate [Beil. II-549, II<sub>1</sub>-(238), II<sub>2</sub>-(511)], oil, h.p. 133° dec., accompanied by a little diethyl di-imino-oxalate [Beil. II-547, II<sub>1</sub>-(238)], m.p. 38°, b.p. 172° strong dec.; in aq. alc., however, the same components give (13) diethyl iminocarbonate [Beil. III-37, III<sub>1</sub>-(18), III<sub>2</sub>-(31)], oil, b.p. 141° cor., accompanied by diethyl di-iminoxalate (see above).]

$\bar{\text{C}}$  with organic reactants. [ $\bar{\text{C}}$  with EtOH (1:6130) yields (8) acetaldehyde (1:0100), acetaldehyde diethylacetal (1:0156), and paraldehyde (1:0170). —  $\bar{\text{C}}$  with acetaldehyde (1:0100) at 0° followed by distn. of the mixture with anhyd. oxalic acid yields (3) chloroacetaldehyde (3:7212).]

[ $\bar{\text{C}}$  with acetone (1:5400) yields (3) chloroacetone (3:5425);  $\bar{\text{C}}$  with methyl phenyl ketone (acetophenone) (1:5515) yields (3)  $\alpha$ -chloroacetophenone (phenacyl chloride) (3:1212);  $\bar{\text{C}}$  with benzaldehyde (1:0195) yields (3) benzoyl chloride (3:6240).]

[ $\bar{\text{C}}$  with phenol in  $\text{CCl}_4$  yields (3) both *o*-chlorophenol (3:5980) and *p*-chlorophenol

(3:0475);  $\bar{C}$  with hydroquinone (1:1590) in ether gives (3) 2,3-dichlorohydroquinone (3:4220).]

$\bar{C}$  with phenyl MgBr in ether at 0° gives (60% yield (14)) (1) chlorobenzene (3:7903). [ $\bar{C}$  with phenylacetylene (1:7425) in  $CCl_4$  yields (3)  $\omega, \omega$ -dichloroacetophenone (3:6835).]

$\bar{C}$  with cyclohexene (1:8070) in  $CCl_4$  yields (3) 2-chlorocyclohexanol-1 (3:0175); for reactn. of  $\bar{C}$  with indene (1:7522) or with 1,4-dihydronaphthalene see (3).]

[ $\bar{C}$  with olefins adds to the unsatd. linkage to give chlorohydrin ethyl ethers (a process now generically designated as chloroalkoxylation): e.g.,  $\bar{C}$  with ethylene yields (15) (17)  $\beta$ -chloroethyl ethyl ether (ethylene chlorohydrin ethyl ether) (3:7463);  $\bar{C}$  with amylene gives (3) a corresp. prod.; the rate of addn. of  $\bar{C}$  to olefins increases from ethylene to amylene (18). — For extensive studies on the prepn. of chlorohydrin ethers from olefins by use of alic. + *N,N*-dichlorobenzenesulfonamide (which mixture appears to generate  $ROCl$  as the active addn. agent) see (18) (19) (20) (21).]

[ $\bar{C}$  has, however, but slight tendency to add to unsaturated acids: e.g.,  $\bar{C}$  in  $CCl_4$  has no actn. (22) on cinnamic acid (1:0735);  $\bar{C}$  in dry ether or  $CCl_4$  with crotonic acid (1:0425) or sorbic acid gives only traces (23) of the expected prods. —  $\bar{C}$  in  $CCl_4$  with hexen-3-oid acid-1 (hydrosorbic acid) [Beil. II-435, II-1(193), II-2(404)] gives addn. to extent of 92% in 3 days (23), but the prod. is not a chloro-ethoxy-hexanoic acid and consists entirely of a mixt. of two stereoisomeric  $\beta$ -chlorohexanoic lactones.]

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3:7025 2-CHLOROPROPANE  
(Isopropyl chloride)



$C_3H_7Cl$

Beil. I - 105

I<sub>1</sub> - (34)

I<sub>2</sub> - (72)

B.P.

F.P.

36-37° (1)  
36.5° at 760 mm. (2) (5)  
36.2-36.5° u.c. (3)  
36.25° (4)  
36.0° at 760 mm. (6)  
35.5° at 757 mm. (7)  
34.8 at 760 mm. (8)  
34.5° at 740 mm. (13)

-117.0° (S)

$D_4^{25} = 0.84281$  (S)

$D_4^{20} = 0.86168$  (S)

0.8610 (7)

$D_4^{15} = 0.86797$  (3)

$n_D^{20} = 1.377$  (17)

$n_D^{15} = 1.38110$  (S)

Colorless limpid liquid with not unpleasant odor. — Alm. insol. aq. [for precise data see (9) (10) (11).] — [For use as refrigerant see (12).]

$\bar{C}$  with MeOH, b.p. 64.7°, forms const.-boilg. mixt., b.p. 33.4°, contg. 94 wt. %  $\bar{C}$  (4);  $\bar{C}$  with EtOH, b.p. 78.3°, forms const.-boilg. mixt., b.p. 35.6°, contg. 97.2 wt. %  $\bar{C}$  (4) [for other azeotropes see Beil. I<sub>2</sub>-(72).]

[For prepn. of  $\bar{C}$  from propanol-2 (1:6135) with conc. HCl + ZnCl<sub>2</sub> (yield: 70-76% (13)) (14) (15) (16) (17) (43); with PCl<sub>3</sub> + ZnCl<sub>2</sub> (74% yield (15)); with PCl<sub>5</sub> + ZnCl<sub>2</sub> (66% yield (15)); with SOCl<sub>2</sub> + pyridine (80% yield (15)); or with AlCl<sub>3</sub> (70% yield (18)) see indic. refs.; for prepn. from propylene by addn. of HCl under various conditions see (19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30).]

[For formn. of  $\bar{C}$  (together with other products) by actn. of Cl<sub>2</sub> on propane see (31), for further actn. of Cl<sub>2</sub> on  $\bar{C}$  see (3).] — [For isomerization of 1-chloropropane to  $\bar{C}$  in presence of metallic catalysts see 1-chloropropane (3:7040).] — [For purification of  $\bar{C}$  with conc. H<sub>2</sub>SO<sub>4</sub> see (32).]

$\bar{C}$  on hydrolysis yields propanol-2 (1:6135). [For study of this reactn. see (2); for use in mfg. of propanol-2 see (33).]

[For reactn. of  $\bar{C}$  with KI in acetone see (1).]

$\bar{C}$  with Mg in dry ether gives (90% yield (17), 93.9% (44)) RMgCl (for reactions of this see below).

[For study of behavior of  $\bar{C}$  with C<sub>6</sub>H<sub>6</sub> or toluene in pure HCl under press. see (45); for behavior with C<sub>6</sub>H<sub>6</sub> + Al/Hg see (46).]

⑤ Isobutyranilide: m.p. 105° (34); 104-105° (35); u.c. (36); 103° cor. (37). [From  $\bar{C}$  (36) or from isopropyl bromide (37) via conversion to RMgX and reactn. with phenyl isocyanate.]

— Isobutyryl-*p*-toluidide: m.p. 103.5-109.5° (38); 106-106.5° (39). [Presumably similarly obtainable via RMgCl + *p*-tolyl isocyanate but not actually so recorded.]

— Isobutyryl- $\alpha$ -naphthalide: unrecorded.

— *S*-(Isopropyl)isothiourea picrate: m.p. 196° (40). [From isopropyl bromide on btg. 3 hrs. in alc. with thiourea, then adding PhOH (40), but not recorded from  $\bar{C}$ .]

— Isopropyl mercuric chloride (sec-PrHgCl): m.p. 97° (47). [Reported only by indirect means (47).]

— *N*-(Isopropyl)phthalimide (2-(*N*-phthalimido)propane): m.p. 86° (48), 85° (49). [Not reported from  $\bar{C}$  but obtd. from isopropyl bromide with K phthalimide in s.t. at 160-170° for 7 hrs. (49), also indirectly (48) (50).]

— *N*-(Isopropyl)-3-nitrophthalimide: unreported.

— *N*-(Isopropyl)tetrachlorophthalimide: unreported.

— *N*-(Isopropyl)-*o*-sulfobenzoic imide (*N*-isopropylsaccharin): m.p. 134° (51). [Not reported from  $\bar{C}$  but obtd. from either isopropyl bromide or isopropyl iodide with aq. sodium saccharin in aq. butylcarbitol (1:6517) on refluxing 30 mm. (51).]

— *N*-(Isopropyl)-*N*-(*p*-bromobenzenesulfonyl)-*p*-anisidine: m.p. 107° u.c. (52). [Not reported from  $\bar{C}$  but obtd. from isopropyl bromide with *N*-(*p*-bromobenzenesulfonyl)-*p*-anisidine in alc. KOH (52).]

— *p*-Isopropoxybenzoic acid: m.p. 160-163° (53). [From  $\bar{C}$  (?) or from isopropyl bromide with ethyl *p*-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (53).]

— Isopropyl 2,4,6-triiodophenyl ether: m.p. 43° cor. (41). [From isopropyl bromide on refluxing with 2,4,6-triiodophenol, m.p. 157-158°, in alc. NaOEt (41).]

— Isopropyl  $\alpha$ -naphthyl ether: b.p. 282.5° cor. (42) [picrate: m.p. 104.5-105.5° cor. (42)].

— Isopropyl  $\beta$ -naphthyl ether: b.p.  $285^\circ$  cor., m.p.  $40.0^\circ$  cor. (42) [picrate: m.p.  $95.0-95.5^\circ$  cor. (42)].

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### 3: 7030 1-CHLOROPROPENE-1

(Propenyl chloride,  
 $\beta$ -methylvinyl chloride)



$\text{C}_3\text{H}_5\text{Cl}$

Beil. I - 198

$I_1$ —

$I_2$ —

trans form

B.P.

$37.4^\circ$  at 760 mm. (1)

$36.7^\circ$  at 747 mm. (2)

F.P.

$-90^\circ$  (1)

$n_D^{20} = 1.4054$  (2)

cis form

B.P.

$32.8^\circ$  at 760 mm. (1)

$32.0-32.2^\circ$  at 747 mm. (2)

F.P.

$-134.8^\circ$  (1)

$n_D^{20} = 1.4053$  (2)

Mobile colorless liq. lighter than water (3).  $\bar{C}$  is stable toward hydrolysis; for use in anal. of mixts. of  $\bar{C}$  with 3-chloropropene-1 (allyl chloride) (3:7035) see (7).

[For prepn. of  $\bar{C}$  from 1,1-dichloropropane (3:7230) + alc. KOH in s.t. at 100° (3) (4) or with alc. NaOEt (2) see indicated refs.; for formn. from 1,2-dichloropropane (propylene dichloride) (3:5200) + alc. KOH see (3) (5) ( $\bar{C}$  is principal product (5), but some 2-chloropropene-1 (3:7020) and propadiene are also formed); for formn. of *cis* isomer from  $\alpha,\beta$ -dichloro-*n*-butyric acid of m.p. 62.5–63° by warming with  $\text{Na}_2\text{CO}_3$  see (6).]

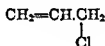
$\bar{C}$  with  $\text{Br}_2$  at  $-15^\circ$  yields 1-chloro-1,2-dibromopropane, b.p. 177–177.5° cor. (3).

$\bar{C}$  in presence of nir or added peroxides adds HBr rapidly to give exclusively (2) 1-chloro-2-bromopropane, b.p. 117.2–117.3° at 740 mm., 52.0° at 75 mm.,  $n_D^{20} = 1.4795$  (2).

[For study of molecular refraction and dipole moment of both *cis* and *trans* forms of  $\bar{C}$  see (8).]

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3:7035 3-CHLOROPROPENE-1  
(Allyl chloride)



Beil. I - 198

I<sub>1</sub>-(82)

I<sub>2</sub>-(100)

B.P.

F.P.

40.0–47.5° at 772.5 mm. (1)

–134.5° (7)

$D_4^{25} = 0.03100$  (7)

46–47° at 768 mm. (2)

–130.4° (10)

$D_4^{20} = 0.9379$  (14)

46.0–40.5° (3)

(4)

0.03764 (7)

46° (4)

(5)

0.0374 (11)

45.7° at 760 mm. (5)

(1)

0.0207 (9)

45.5–47° at 766.9 mm. (1)

(6)

$D_4^{15} = 0.04410$  (7)

45.36° (6)

(7)

45.1° at 760 mm. (7)

(103)

$n_D^{20} = 1.41538$  (14)

44.0° at 751 mm. (103)

(8) (61)

1.4151 (11)

44.8–45.0° at 756.2 mm. (8) (61)

(9)

1.40950 (9)

44.8° at 754 mm. (9)

(10)

44.6° at 760 mm. (10)

(11) (12)

$n_D^{15} = 1.41883$  (7)

44.6° (11) (12)

(13)

44.5–44.7° at 744 mm. (13)

(14)

44.4–44.6° - (14)

Colorless oil, spnr. sol. aq.; volatile with steam.

$\bar{C}$  with EtOH (1:6130) forms a const.-boilg. mixt., b.p. 44° at 760 mm., contg. 95%  $\bar{C}$  (5); with formic acid (1:1005) forms a const.-boilg. mixt., h.p. 45.0° nt 760 mm., contg. 92.5%  $\bar{C}$  (15).

$\bar{C}$  is one of most toxic of all halohydrocarbons (for study see (16)).

[For prepn. of  $\bar{C}$  from allyl alcohol (1:6144) + conc. HCl in s.t. at 100° for 3 hrs. (17), with conc. HCl (1) (23) or 10 days nt room temp. (55–6 N HCl (50% yield (19)), with  $\text{ZnCl}_2$  or dislvd. in cold conc. HCl and treated with  $\text{Cu}_2\text{Cl}_2$  (small amt.) + conc.  $\text{H}_2\text{SO}_4$  (yield 85–90% (2), 80% (22)) see indic. refs.; from allyl alcohol (1:6145) with  $\text{SOCl}_2$  in  $\text{C}_6\text{H}_6$

(71% yield (21)), with  $\text{PCl}_3$  (1) (24), with  $\text{PCl}_3 + \text{ZnCl}_2$  in  $\text{C}_6\text{H}_6$  at  $0^\circ$  (63% yield (21)), with  $\text{PCl}_3 + \text{pyridine}$  (73% yield (9)), with  $\text{PCl}_3 + \text{ZnCl}_2$  in  $\text{C}_6\text{H}_6$  (57% yield (21)) see indic. refs.]

[For prepn. of  $\bar{\text{C}}$  from allyl formate (1:3035) with conc.  $\text{HCl} + \text{a little } \text{Cu}_2\text{Cl}_2 + \text{conc. } \text{H}_2\text{SO}_4$  (93–98% yield (22)), or with  $\text{ZnCl}_2 + \text{HCl}$  gas (80–90% yield (25)) (26) see indic. refs.; from allyl oxalate in alc.  $\text{CaCl}_2$  in s.t. at  $100^\circ$  see (27); from allyl iodide with alc.  $\text{HgCl}_2$  at ord. temp. see (27).]

[For comml. prepn. of  $\bar{\text{C}}$  from propylene with  $\text{Cl}_2$  at elevated temps., e.g.,  $500^\circ$  (yield 96%  $\bar{\text{C}}$  accompanied by 3% 2-chloropropene-1 (3:7020) + 1% mixed *cis* and *trans* isomers of 1-chloropropene-1 (3:7030) (11)) (28) (29), see indic. refs. (note also that the high-boiling material from distn. of comml.  $\bar{\text{C}}$  contains (110) approx. 60% 1,3-dichloropropene-1 (3:5250) + 30% 1,2-dichloropropane (3:5200)); for examples of patents covering this procedure see (30) (31) (32) (33) (34) (35), from propane (34) (36) or 1-chloropropane (3:7040) (36) with  $\text{Cl}_2$  + cat. at  $500\text{--}700^\circ$  see indic. refs.; from 1,2-dichloropropane (3:5200) by suitable pyrolysis (yield: 55–70%  $\bar{\text{C}}$  + 30–40% of mixt. of *cis* and *trans* isomers of 1-chloropropene-1 (3:7030) + 5% 2-chloropropene-1 (3:7020) (11)) cf. (12) (13) (39); for examples of relevant patents see (37) (38) (40).]

Reactions involving the double bond of  $\bar{\text{C}}$ . [ $\bar{\text{C}}$  with  $\text{Cl}_2$  adds and/or substitutes according to conditions (for study of relative proportions of these reactions see (29) (11));  $\bar{\text{C}}$  with  $\text{Cl}_2$  at ord. temp. (41) or  $\bar{\text{C}}$  with  $\text{SO}_2\text{Cl}_2$  in  $\text{CCl}_4$  in pres. of peroxides (42) gives (80–90% yield (42)) 1,2,3-trichloropropane (3:5840) (note that this comprises one step in one of the modern syntheses of glycerol from petroleum (43) (44));  $\bar{\text{C}}$  with  $\text{Cl}_2$  at high temp. yields (11) a mixt. of prods. of which the dichloropropene fraction comprises (11) 47% 1,3-dichloropropene-1 (high-boilg. isomer) (3:5250) + 42% 1,3-dichloropropene-1 (low-boilg. isomer) (3:5250) + 11% 1,1-dichloropropene-2 (3:5140) + trace of 1,2-dichloropropene-2 (3:5190).]

[ $\bar{\text{C}}$  with  $\text{Br}_2$  adds 1 mole of halogen yielding (45) mainly 1,2-dibromo-3-chloropropane ( $\gamma$ -chloropropylene dibromide) [Beil. I-111], b.p.  $195^\circ$  (45); for study of rate of addn. of  $\text{Br}_2$  under various conditions see (14) (9) (46) (105); for heat of reactn. see (47).]

[ $\bar{\text{C}}$  with conc. aq.  $\text{HCl}$  in s.t. at  $100^\circ$  for 18 hrs. (48), or  $\bar{\text{C}}$  with dry  $\text{HCl}$  in dark at  $0^\circ$  in absence of  $\text{FeCl}_3$  (33% yield (49)) or at room temp. in pres. of  $\text{FeCl}_3$  (85–89% yield (49)), gives 1,2-dichloropropane (propylene dichloride) (3:5200); note that addn. of  $\text{HCl}$  is not complicated by a peroxide effect but is very slow unless  $\text{FeCl}_3$  (or less advantageously  $\text{AlCl}_3$ ) is used as a cat. (49). —  $\bar{\text{C}}$  satd. with  $\text{HBr}$  gas at  $0^\circ$  or below (50), or with conc. aq.  $\text{HBr}$  at  $0^\circ$  (51), or with  $\text{HBr}$  gas in s.t. at  $100^\circ$  for 8 hrs. (45) cf. (52), or in presence of  $\text{Fe}$  (53) or other cat., e.g.,  $\text{BiCl}_3$  (54), as directed, gives (yields: 36–38% (53), 43% (52), 50% (51), 87% (50)) 1-bromo-3-chloropropane ( $\gamma$ -chloro- $n$ -propyl bromide) (trimethylene chlorobromide) [Beil. I-109, I<sub>1</sub>-(36), I<sub>2</sub>-(75)], b.p.  $142^\circ$ ; note that the above mode of addn. is favored by peroxides (49) (54) cf. (106). —  $\bar{\text{C}}$  with  $\text{HI}$  (10–20% excess at  $0^\circ$ ) gives exclusively (90–100% yield (55)) 1-chloro-2-iodopropane, b.p.  $66.2^\circ$  at 50 mm.,  $n_D^{20} = 1.5472$  (55); note that in this reactn. formn. of 2-iodopropane (isopropyl iodide) has also been reported (56)]

[ $\bar{\text{C}}$  (1 mole) with conc.  $\text{H}_2\text{SO}_4$  (2 moles) at  $0^\circ$  gives an oily addn. prod. (24) (presumably  $\beta$ -chloroisopropyl hydrogen sulfate) which upon dilution with aq. and subsequent distillation gives (50% yield (57) (61)) (24) (58) (59) (60) 1-chloropropanol-2 (3:7747); in pres. of  $\text{CuSO}_4$  the yield rises to 66–70% (62). —  $\bar{\text{C}}$  adds  $\text{HOCl}$  yielding (63) (64) (65) (76) 2,3-dichloropropanol-1 (glycerol  $\beta$ -dichlorohydrin) (3:6060). —  $\bar{\text{C}}$  with *ter*-butyl hypochlorite (3:7165) in  $\text{MeOH}$  contg. a little *p*-toluenesulfonic acid gives at  $40^\circ$  (44% yield (66)) 1,3-dichloro-2-methoxypropane ( $\beta,\beta'$ -dichloroisopropyl methyl ether), b.p.  $154\text{--}156^\circ$  at 730 mm.,  $D_4^{20} = 1.2235$ ,  $n_D^{20} = 1.4542$  (66)]

[ $\bar{C}$  with liq.  $SO_2$  + trace of ascaridole + a few drops of aq. or alc.  $HCl$ ,  $HBr$ , or  $H_2SO_4$  gives (70–100% yield (67)) cf. (68) allyl chloride polysulfone, no def. m.p., dec. 210–235°, sol.  $CHCl_3$  or acetone but insol. most other org. solvents; note, however, that this addn. of  $SO_2$  is completely inhibited by the pres. of as little as 5 mole % of allyl bromide or cinnamyl bromide (67). —  $\bar{C}$  (2 moles) with  $S_2Cl_2$  (1 mole) in s.t. at 100° for 6 hrs. deposits sulfur and yields (69) bis-( $\beta$ , $\gamma$ -dichloro-*n*-propyl) sulfide, pale yel. oil, b.p. 181–182° at 15 mm. (69); the same components maintained at room temp. for 10 days, however, deposit no sulfur and on distn. yield (69) bis-( $\beta$ , $\gamma$ -dichloro-*n*-propyl) disulfide, b.p. 190° at 11 mm. (69).]

[ $\bar{C}$  (2 moles) with cyclopentadiene (1 mole) (1:8030) in s.t. at 170–180° for 8 hrs. gives (74% yield on  $C_5H_6$  (70)) by Diels-Alder addn. 2,5-endomethylene-1,2,5,6-tetrahydrobenzyl chloride (1-(chloromethyl)-2,5-endomethylenecyclohexene-3), b.p. 54–57° at 11 mm. (70). — For polymerization of  $\bar{C}$  see (71) (101).]

[ $\bar{C}$  with excess diazomethane in ether stood for 3 days yields a yel. very hygroscopic ppt. presumably 3-(chloromethyl)- $\Delta^2$ -pyrazoline (72).]

[ $\bar{C}$  with  $C_6H_6$  + conc.  $H_2SO_4$  gives (73) by addn. to the ethylene linkage  $\beta$ -chloro-*n*-propylbenzene (2-chloro-1-phenylpropane) [Beil. V-391,  $V_1$ -(189),  $V_2$ -(304)], b.p. 85° at 13 mm.,  $D_4^{19} = 1.047$ ,  $n_D^{19} = 1.5245$  (73); note, however, that  $\bar{C}$  with  $C_6H_6$  in pres. of  $FeCl_3$  at –20° gives (33.5% yield (74)) (73) the isomeric ( $\beta$ -chloroisopropyl)benzene (1-chloro-2-phenylpropane) [Beil.  $V_1$ -(191)], b.p. 79° at 10 mm.,  $D_4^{17} = 1.0367$ ,  $n_D^{16} = 1.52129$  (74);  $\bar{C}$  with  $C_6H_6$  +  $AlCl_3$  ( $\frac{1}{2}$  mole) gives none of the  $\beta$ -chloroisopropylbenzene since it apparently reacts with more  $C_6H_6$  yielding (74)  $\alpha$ -methylbibenzyl (1,2-diphenylpropane [Beil. V-613,  $V_1$ -(288),  $V_2$ -(517)].] [For analogous condensation of  $\bar{C}$  with fluorobenzene, chlorobenzene (3:7903), and bromobenzene see (118).]

[For oxidn. of  $\bar{C}$  in liq. phase at 75–250° by  $O_2$  in pres. of  $Cu(OAc)_2$  or peroxide catalysts and in an org. solv. such as  $AcOH$  to hydroxylated cpds. see (75).]

Reactions involving the halogen atom of  $\bar{C}$ . [ $\bar{C}$  +  $H_2$  over activated charcoal at 300–500° gives (58% yield (77)) propylene; note that the double bond is not (77) hydrogenated.]

[ $\bar{C}$  passed over activated charcoal contg. 1–2%  $KOH$  is dehalogenated (78) at 375° to extent of 21%; at 400°, 58%.]

[ $\bar{C}$  with aq. vapor at 550–850° + cat. (79) or under press. with alkali hydroxides (80) or with  $HCl/Cu_2Cl_2$  (108) yields (cf. (43) (44)) allyl alcohol (1:7145). —  $\bar{C}$  with alc.  $KOH$  (81) (107) or alc.  $NaOH$  (12) yields allyl ethyl ether (1:7850) + alkali chloride; for use of this reactn. in detn. of  $\bar{C}$  in pres. of *cis*-1-chloropropene-1 (3:7030) and *trans*-1-chloropropene-1 (3:7030) see (12); for study of rate of reactn. of  $\bar{C}$  with  $NaOMe$  at 16–18° (82) or of  $\bar{C}$  with  $NaOEt$  at 35° and 50° (83) see indic. refs.]

[ $\bar{C}$  with alc.  $KSH$  gives mainly (84) di-allyl sulfide [Beil. I-441,  $I_1$ -(226),  $I_2$ -(478)], b.p. 138–139° (84).] — [For reactn. of  $\bar{C}$  with alkali polysulfides in prepn. of rubber-like prod. see (85).]

[For studies of rate of reactn. of  $\bar{C}$  with  $KI$  in acetone at 20° (83), 25° (86), or 60° (87) cf. (9) see indic. refs.; for reactn. of  $\bar{C}$  with  $Na_3AsO_3$  yielding allylarsinic acid see (88); for reactn. of  $\bar{C}$  with  $CuCN$  giving (85% yield (22)) allyl cyanide (vinylacetoneitrile) [Beil. II-408,  $II_1$ -(187),  $II_2$ -(389)], b.p. 117.8–118.2° at 757 mm. (22), see indic. refs.; for reactn. of  $\bar{C}$  with  $Mg$  + acetone, giving allyl-dimethyl-carbinol [Beil. I-445,  $I_2$ -(487)], b.p. 118–120°,  $D_4^{17} = 0.83452$ ,  $n_D^{17} = 1.4300$  see (89).]

[ $\bar{C}$  with conc. aq.  $NH_4OH$  as directed (90) yields allylamine [Beil. IV-205,  $IV_1$ -(389),  $IV_2$ -(662)], b.p. 56°, misc. aq. — For study of rate of addn. of  $\bar{C}$  to pyridine or reactn. with piperidine see (82) (91); for sepn. of  $\bar{C}$  from other chloro-olefins, e.g., 1-chloropropene-1 (3:7030) or 2-chloropropene-1 (3:7020), by conv. of  $\bar{C}$  to quaternary salt see (111).]

$\bar{C}$  with  $Mg$  in dry ether under carefully regulated conditions gives (84% yield (102))

cf. (109) (119) allyl MgCl; note that if this prod. reacts with phenyl isocyanate in a fashion analogous (103) to allyl MgBr the prod. obtd. should be crotonanilide, m.p. 113-114° cor. (103).

( $\bar{C}$  with Mg in dry ether as directed gives (63% yield crude, 27% pure (92), 60% (93)) hexadiene-1,5 (1:8045). —  $\bar{C}$  with NaNH<sub>2</sub> in liq. NH<sub>3</sub> as directed gives (30% yield (94)) hexatriene-1,3,5 (Beil. I-263, I<sub>2</sub>(243)), b.p. 76-80°,  $D_4^{20} = 0.7182$ ,  $n_D^{20} = 1.4330$  (94); during the reactn. an intermediate chlorohexadiene (95), b.p. 115° at 748 sl. dec., 46-47.5° at 96 mm.,  $n_D^{20} = 1.4483$ , appears to be formed, and the hexatriene is accompanied (94) (95) by variable amts. of its dimer, trimer, and tetramer. — For reaction of  $\bar{C}$  with monosodium acetylene in liq. NH<sub>3</sub> see (96).]

( $\bar{C}$  with 1-chloro-2-methylpropene-2 (methallyl chloride) (3:7145) + Mg in ether gives (93) 47% 2-methylhexadiene-1,5 (b.p. 88.1° at 760 mm.,  $D_4^{20} = 0.7198$ ,  $n_D^{20} = 1.4184$ ) + 30% 2,5-dimethylhexadiene-1,5 (b.p. 114.3° at 760 mm.,  $D_4^{20} = 0.7423$ ,  $n_D^{20} = 1.4293$ ) + 12% hexadiene-1,5 (biallyl) (1:8045). —  $\bar{C}$  with crotyl chloride (the equil. mixt. of 1-chlorobutene-2 (3:7205) and 3-chlorobutene-1 (3:7090)) + Mg in ether gives 34% heptadiene-1,5 (b.p. 93.7° at 760 mm.,  $D_4^{20} = 0.7186$ ,  $n_D^{20} = 1.4200$ ) + 21% 3-methylheptadiene-1,5 (b.p. 111.0° at 760 mm.,  $D_4^{20} = 0.7291$ ,  $n_D^{20} = 1.4240$ ) + 10% hexadiene-1,5 (1:8045) + 10% 3-methylhexadiene-1,5 (b.p. 80.0° at 760 mm.,  $D_4^{20} = 0.7103$ ,  $n_D^{20} = 1.4116$ ) + 1% octadiene-1,6 (b.p. 124.5° at 760 mm.,  $D_4^{20} = 0.7441$ ,  $n_D^{20} = 1.4336$ ) (93).]

[ $\bar{C}$  reacts with RMgX cpds. in normal coupling; e.g.,  $\bar{C}$  with EtMgBr gives (97) pentene-1 (1:8205);  $\bar{C}$  with *n*-PrMgBr gives (97) hexene-1 (1:8255);  $\bar{C}$  + *n*-C<sub>8</sub>H<sub>17</sub>MgCl gives (80% yield (93)) octene-1 (1:8375);  $\bar{C}$  with iso-AmMgCl gives (60% yield (93)) 6-methylheptene-1 (b.p. 113.2° at 760 mm.,  $D_4^{20} = 0.7119$ ,  $n_D^{20} = 1.4068$ );  $\bar{C}$  with *o*-tolyl MgBr gives (98) *o*-allyltoluene (b.p. 182-183° at 757 mm.,  $D_4^{20} = 0.9001$ ,  $n_D^{20} = 1.5186$ ).]

Miscellaneous reactions of  $\bar{C}$ . [ $\bar{C}$  with phenol (1:1420) + conc. H<sub>2</sub>SO<sub>4</sub> stood at room temp. for 6 months gives (99) *o*-isopropenylphenol [Beil. VI-572, VI<sub>1</sub>-(233)]; for analogous prods. from  $\bar{C}$  with *o*-cresol (1:1400), *m*-cresol (1:1730), and *p*-cresol (1:1410) see (99).]

⊙ *S*-Allylthiourea picrate: m.p. 155° (100). [From  $\bar{C}$  thiourea in EtOH, refluxed for 5 min., treated with PhOH (100).]

— *N*-(Allyl)phthalimide [Beil. XXI-464, XXI<sub>1</sub>-(364)]: m.p. 70°. [The direct prepn. of this cpd. from  $\bar{C}$  has not been reported; it has, however, been obtd. from allyl bromide with K phthalimide in s.t. at 150° for 2-3 hrs. (50% yield (104)) and has also been prepd. by numerous indirect means; with Cl<sub>2</sub> in CHCl<sub>3</sub> it yields *N*-(β,γ-dichloro-*n*-propyl)phthalimide, ndls. from alc., m.p. 93° (104); with Br<sub>2</sub> in CHCl<sub>3</sub> it yields *N*-(β,γ-dibromo-*n*-propyl)phthalimide, m.p. 113-114° (104).]

— *N*-(Allyl)-3-nitrophthalimide: pl. from CS<sub>2</sub>, m.p. 100-101° (112). [Not reported from  $\bar{C}$  but obtd. from allyl bromide with K 3-nitrophthalimide (112), for photographs of cryst. see (113).]

— *N*-(Allyl)tetrachlorophthalimide: unreported.

⊕ *N*-(Allyl)-*o*-sulfobenzoic imide (*N*-allylsaccharin): m.p. 58° (114). [From  $\bar{C}$  with sodium saccharin in aq. butylcarbitol (1:6517) on refluxing 30 min. (114).]

— *N*-(Allyl)-*N*-(*p*-bromobenzenesulfonyl)-*p*-aniside: m.p. 82° u.c. (115). [Not reported from  $\bar{C}$  but obtd. from allyl bromide with *N*-(*p*-bromobenzenesulfonyl)-*p*-anisidine in alc. KOH (115).]

— *p*-Allyloxybenzoic acid: m.p. 162-163° u.c. (116). [From  $\bar{C}$  (?) or from allyl bromide with ethyl *p*-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (116); note, however, that m.p. of prod. is almost identical with corresp. deriv., m.p. 160-163°, from isopropyl halides.]



- Allyl  $\alpha$ -naphthyl ether: m.p.  $-10^{\circ}$  (117) (corresp. picrate, m.p.  $100.5-101.0^{\circ}$  cor. (117)).
- Allyl  $\beta$ -naphthyl ether: m.p.  $+16^{\circ}$  (117) (corresp. picrate, m.p.  $98.5-99.0^{\circ}$  cor. (117)).

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### 3:7040 1-CHLOROPROPANE (*n*-Propyl chloride)



Beil. I - 104

I<sub>1</sub>- (34)

I<sub>2</sub>- (72)

B.P.

F.P.

46.60°	at 760 mm.	(1)	-122.8° (1) (7)	$D_4^{25} = 0.88611$	(1)
46.6°	at 770.5 mm.	(2)		$D_4^{20} = 0.89220$	(1)
46.3-46.7° u.c.		(3)		0.8890	(52)
46.4° cor.	at 760 mm.	(4) (5)		$D_4^{15} = 0.89486$	(1)
46.0-46.5°	at 764 mm.	(52)		$n_D^{20} = 1.38856$	(8)
45.70-45.75°	at 760 mm.	(6)		1.38838	(9)
44°	at 744 mm.	(8)		1.38800	(52)

Colorless limpid liquid with not unpleasant odor. — Almost insol. aq. [for precise data see (10) (11) (12)].

$\bar{C}$  with MeOH, b.p. 64.7°, forms const.-boilg. mixt., b.p. 40.5°, contg. 90.5 wt. %  $\bar{C}$  (13);  $\bar{C}$  with EtOH, b.p. 78.3°, forms const.-boilg. mixt., b.p. 45.0°, contg. 94 wt. %  $\bar{C}$  (14);  $\bar{C}$  with isopropyl alc., b.p. 82.5°, forms const.-boilg. mixt., b.p. 46.4°, contg. 97.2 wt. %  $\bar{C}$  (14);  $\bar{C}$  with CS<sub>2</sub>, b.p. 46.3°, forms const.-boilg. mixt., b.p. 42.05°, contg. 44.5 wt. %  $\bar{C}$  (14). — [For f.p./compn. data on mixts. of  $\bar{C}$  with cyclohexyl chloride (3:8040) or with isopropyl bromide see (15).]

[For prepn. of  $\bar{C}$  from propanol-1 (1:6150) with conc.  $HCl$  (16), 70–72% (16), 65–70% (17), 61% (18) (19)); with  $PCl_5$  (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30) (31) (32) (33) (34) (35) (36) (37) (38) (39) (40) (41) (42) (43) (44) (45) (46) (47) (48) (49) (50) (51) (52) (53) (54) (55) (56) (57) (58) (59) (60) (61) (62) (63) (64) (65) (66) (67) (68) (69) (70) (71) (72) (73) (74) (75) (76) (77) (78) (79) (80) (81) (82) (83) (84) (85) (86) (87) (88) (89) (90) (91) (92) (93) (94) (95) (96) (97) (98) (99) (100); with  $PCl_5$  (5) +  $ZnCl_2$  (76% yield (19)); with  $SOCl_2$  + refs.; for other misc. methods see Beil.]

[For formn. of  $\bar{C}$  (together with  $\bar{C}$ ) (1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11) (12) (13) (14) (15) (16) (17) (18) (19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30) (31) (32) (33) (34) (35) (36) (37) (38) (39) (40) (41) (42) (43) (44) (45) (46) (47) (48) (49) (50) (51) (52) (53) (54) (55) (56) (57) (58) (59) (60) (61) (62) (63) (64) (65) (66) (67) (68) (69) (70) (71) (72) (73) (74) (75) (76) (77) (78) (79) (80) (81) (82) (83) (84) (85) (86) (87) (88) (89) (90) (91) (92) (93) (94) (95) (96) (97) (98) (99) (100); for further actn. of  $Cl_2$  on  $\bar{C}$  (1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11) (12) (13) (14) (15) (16) (17) (18) (19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30) (31) (32) (33) (34) (35) (36) (37) (38) (39) (40) (41) (42) (43) (44) (45) (46) (47) (48) (49) (50) (51) (52) (53) (54) (55) (56) (57) (58) (59) (60) (61) (62) (63) (64) (65) (66) (67) (68) (69) (70) (71) (72) (73) (74) (75) (76) (77) (78) (79) (80) (81) (82) (83) (84) (85) (86) (87) (88) (89) (90) (91) (92) (93) (94) (95) (96) (97) (98) (99) (100); for isomerization of  $\bar{C}$  (1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11) (12) (13) (14) (15) (16) (17) (18) (19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30) (31) (32) (33) (34) (35) (36) (37) (38) (39) (40) (41) (42) (43) (44) (45) (46) (47) (48) (49) (50) (51) (52) (53) (54) (55) (56) (57) (58) (59) (60) (61) (62) (63) (64) (65) (66) (67) (68) (69) (70) (71) (72) (73) (74) (75) (76) (77) (78) (79) (80) (81) (82) (83) (84) (85) (86) (87) (88) (89) (90) (91) (92) (93) (94) (95) (96) (97) (98) (99) (100); for isomerization of  $\bar{C}$  accompanying alkylation see (29); for  $\bar{C}$  in Friedel-Crafts reactn. see (30).]

[For isomerization of  $\bar{C}$  (1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11) (12) (13) (14) (15) (16) (17) (18) (19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30) (31) (32) (33) (34) (35) (36) (37) (38) (39) (40) (41) (42) (43) (44) (45) (46) (47) (48) (49) (50) (51) (52) (53) (54) (55) (56) (57) (58) (59) (60) (61) (62) (63) (64) (65) (66) (67) (68) (69) (70) (71) (72) (73) (74) (75) (76) (77) (78) (79) (80) (81) (82) (83) (84) (85) (86) (87) (88) (89) (90) (91) (92) (93) (94) (95) (96) (97) (98) (99) (100); for isomerization of  $\bar{C}$  accompanying alkylation see (29); for  $\bar{C}$  in Friedel-Crafts reactn. see (30).]

$\bar{C}$  on passing over various cat. espec. at elevated temps. loses  $HCl$  (30) (31) + Beil. I<sub>2</sub> (72).  
[For study of behavior of  $\bar{C}$  with  $KI$  see (33); toward  $Na$  see (34) (35) (36); with  $Mg$  in dry ether see (37) (note that  $\bar{C}$  with  $Mg$  in dry ether contg. trace of  $I_2$  gives in absence of air 98.2% yield (51)  $RMgCl$ ).]

① *n*-Butyranilide: m.p. 96° (38); 97° (39); 92° cor. (40), u.c. (41). [From  $\bar{C}$  (41) or *n*-propyl bromide (40) via conversion to  $RMgX$  and reactn. with phenyl isocyanate (41).]

— *n*-Butyr-*p*-toluidide: m.p. 75° (38); 74–75° (42); 73–74° (43). [Presumably similarly obtainable via  $RMgCl$  + *p*-tolyl isocyanate, but not actually so recorded.]

② *n*-Butyr- $\alpha$ -naphthalide: m.p. 120° (44); 121° (45). [From  $RMgBr$  via reactn. with  $\alpha$ -naphthyl isocyanate (45).]

— *n*-Propyl mercuric chloride: m.p. 140° (46).

③ *S*-(*n*-Propyl)isothioureia picrate: m.p. 176° (47). [In small yield from  $\bar{C}$  on htg. 5 hrs. with thiourea in alc., followed by addn. of  $PKOH$  (47).]

— *n*-Propyl 2,4,6-triiodophenyl ether: m.p. 82° cor. (48). [From *n*-propyl bromide on refluxing with 2,4,6-triiodophenol, m.p. 157–158°, in alc.  $NaOEt$  (48).] [Note that this ether depresses m.p. of corresp. Et 2,4,6-triiodophenyl ether, m.p. 82° cor. (48).]

— *N*-(*n*-Propyl)-3-nitrophthalimide: ndls. from  $CS_2$ , m.p. 84–85° (49). [From *n*-propyl bromide on refluxing with  $K$  3-nitrophthalimide (49).]

— *n*-Propyl  $\alpha$ -naphthyl ether: h.p. 293.5° cor. (50) [picrate: m.p. 99.5–100° cor. (50)].

— *n*-Propyl  $\beta$ -naphthyl ether: h.p. 297.0° cor., m.p. 39.5–40.0° cor. (50) [picrate: m.p. 80.5–81.5° cor. (50)].

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### 3:7045 2-CHLORO-2-METHYLPROPANE

(*ter*-Butyl chloride;  
trimethylcarbinyl chloride)



$\text{C}_4\text{H}_9\text{Cl}$

Beil. I - 125

I<sub>1</sub>-(40)

I<sub>2</sub>-(88)

B.P.		F.P.		
52°		(1) -24.6° (12)	$D_4^{25} = 0.83537$ (9)	
51.52° cor.		(2) (36) -25.4° (13)	$D_4^{20} = 0.8511$ (20)	
51.6°		(3) -27.1° (9) (10)	0.8467 (16)	
51.0-51.2°		(4) -28.5° (5)	0.84138 (9)	
51°		(5)	$D_4^{15} = 0.84739$ (9)	
50.0°	at 762 mm.	(6)		
50.0°		(7)		
50.8°	at 766 mm.	(8)	$n_D^{20} = 1.38786$ (13)	
50.7°	at 760 mm.	(9)	1.3858 (8)	
50.7°		(10)	1.38564 (16)	
50.6-50.8°	at 766 mm.	(11)	1.3855 (17) (21)	
50.60°		(12) (18) (8)	1.3853 (8)	
50.5°		(13)	1.38528 (10)	
50.0°	at 749 mm.	(14)	1.38470 (12)	
40.7°	at 742.4 mm.	(15)	1.3839 (18)	
49.5°	at 738 mm.	(16)	$n_D^{18} = 1.3860$ (22)	
49-50°		(17)	$n_D^{17.8} = 1.38686$ (1)	

[See also 1-chloro-2-methylpropane (3:7135).]

Binary systems of  $\bar{\text{C}}$  with other org. cpds. — For f.p./compn. data of mixts. of  $\bar{\text{C}}$  with  $\text{CCl}_4$  (3:5100) (23) (13), with *n*-butyl chloride (3:7160) (19), with *n*-butyl bromide (19), or with isobutyl bromide (19) see indic. refs.

$\bar{\text{C}}$  with MeOH (1:6120) forms a const.-boilg. mixt., b.p. 43.75°, contg. 90%  $\bar{\text{C}}$  (24);  $\bar{\text{C}}$  with formic acid (1:1005) forms a const.-boilg. mixt., b.p. 50.0°, contg. 88.8%  $\bar{\text{C}}$  (3);  $\bar{\text{C}}$  with  $\text{CS}_2$  forms a const.-boilg. mixt., b.p. 43.3°, contg. 37%  $\bar{\text{C}}$  (25). — Note that  $\bar{\text{C}}$  gives no azeotrope with *ter*-BuOH (1:6140) (9).

Preparation of  $\bar{\text{C}}$ . [For prepn. of  $\bar{\text{C}}$  from *ter*-BuOH (1:6140) with conc. HCl (3 vols.) by shaking in cold (espec. in pres. of  $\text{CaCl}_2$ ) (78-83% yield (26)) or by distillation (using

7-8 pts. by wt. conc. HCl (94% yield (27)), or with dil. aq. HCl (18-20 B6) in pres. of inorg. halide cat. (28) see indic. refs.]

[For prepn. of  $\bar{C}$  from *ter*-BuOH (1:6140) with dry HCl gas in cold (1) (29), with HCl gas in pres. of pyridine at elevated temp. (some isobutyl chloride (3:7135) is also formed (30)); with  $PCl_3$  (31),  $PCl_3 + ZnCl_2$  (92% yield (32)),  $PCl_5$  (33) (34),  $PCl_5 + ZnCl_2$  (85% yield (32)), or excess  $AlCl_3$  (35); with oxalyl (di)chloride (3:5060) (36) or with trichloromethyl chloroformate (diphosgene) (3:5515) (20) see indic. refs.]

$\bar{C}$  can also be obtained from various isobutyl cpds. (see following paragraphs), but it must be constantly kept in mind that reactns. of this type involve the equilibrium between  $\bar{C}$ , isobutylene, and isobutyl chloride, and the proportions of the two halides may vary widely according to particular conditions; for some types of utilization, however, such a mixture may serve just as well as pure  $\bar{C}$ .

[For prepn. of  $\bar{C}$  from 2-methylpropane (isobutane) with  $Cl_2$  see (37) (38) (39); from isobutylene with HCl gas (40) (41) (4) (18), with conc. aq. HCl (42) (43) (44), with HCl gas +  $AlCl_3$  at  $-50^\circ$  (45), with HCl gas + cat. (46), from tech. cracked gas (contg. isobutylene) with HCl (47) (48) (49) (57), with chloromethyl methyl ether (3:7085) +  $HgCl_2$  (other prods. are also formed (50)), or even with  $Cl_2$  (other prods. also formed) (51) (52) (53) see indic. refs.]

[For prepn. of  $\bar{C}$  from 1-chloro-2-methylpropane (isobutyl chloride) (3:7135) by hgt. at  $306^\circ$  (8%  $\bar{C}$  (54)), or passing vapor over  $BaCl_2$  at  $380-400^\circ$  (40%  $\bar{C}$  (55)), or over suitable cat. at  $200^\circ$  as directed (56); from isobutyl iodide with ICl (58); from isobutylamine with  $NOCl$  in xylene at  $-15^\circ$  (59); from isobutyl alcohol (1:6165) with HCl gas (60) cf. (1), with HCl gas over  $Al_2O_3$  at  $420^\circ$  (61), or with  $PCl_3 + ZnCl_2$  (62) see indic. refs.]

[For formn. of  $\bar{C}$  from 2-chloro-2-methylbutane (*ter*-amyl chloride) (3:7220) by cleavage with  $AlCl_3$  (35) or with anhydrous HF at  $0^\circ$  (10-17% yield (17)) see indic. refs.]

Pyrolysis of  $\bar{C}$ . [ $\bar{C}$  on suitable hgt. dec. into isobutylene + HCl; this begins to occur at  $300^\circ$  even in absence of cat. (63) for study of equilibria involved see (4) (18)]; for study of reactn. over  $ThO_2$  at  $100^\circ$  (64), over pumice at  $400-500^\circ$  (65), or over activated carbon contg. 1-2% KOH (dehalogenation is 19.8% at  $375^\circ$ , 51% at  $400^\circ$  (66)) see indic. refs. — Note that  $\bar{C}$  passed over activated carbon at  $400^\circ$  in pres. of  $H_2$  is 51% dehalogenated but the isobutylene is not reduced (67).]

Further halogenation of  $\bar{C}$ . [ $\bar{C}$  in liq. phase with  $Cl_2$  in light gives (68) a mixt. of chlorination prods. contg. approx. 37% 1,2,3-trichloro-2-methylpropane (3:5885) + 25% 1,1,2-trichloro-2-methylpropane (3:5710) + 21% 1,1,2,3-tetrachloro-2-methylpropane (3:6165) + 10% 1,2-dichloro-2-methylpropane (3:7430) + 6% 1,2,3-trichloro-2-(chloromethyl)propane (3:6335) + a trace of 1,1,1,2-tetrachloro-2-methylpropane (3:4725). —  $\bar{C}$  in vapor phase under reduced press. with  $Cl_2$  in u.v. light or in dark electric discharge (69) or  $\bar{C}$  with  $SbCl_3$  (1 mole) with cooling (34) gives 1,2-dichloro-2-methylpropane (3:7430).]

$\bar{C}$  with  $Br_2$  in pres. of Fe (70) or in liq.  $SO_2$  at room temp. for 14 hrs. (100% yield (72)) evolves HCl and gives 1,2-dibromo-2-methylbutane (isobutylene dibromide) [Beil. I-127, I<sub>1</sub>-(41), I<sub>2</sub>-(90)], b.p.  $149.0^\circ$ .

Reactions of the halogen atom of  $\bar{C}$ . The tertiary chlorine atom of  $\bar{C}$  is very reactive and therefore readily hydrolyzed or alcoholized. —  $\bar{C}$  on shaking with aq. for 24 hrs. at room temp. (6) or  $\bar{C}$  on refluxing with 2 vols. aq. for 8 hrs. (71% hydrolysis (72)) yields *ter*-BuOH (1:6140); note rate of hydrolysis of  $\bar{C}$  is greater in pure aq. than in 5% aq.  $Na_2CO_3$  (72); for use of this facile hydrolysis in removal of  $\bar{C}$  from isobutyl chloride (3:7135) see under latter). [For details of studies of kinetics of hydrol. of  $\bar{C}$  under various circumstances, e.g., in aq. alc., see (73) (74) (75) (6) (11); in formic acid (14) (77) (78).] [For use in prepn. of *ter*-butyl alc. (1:6140) see (79).]

[ $\bar{C}$  (2 moles) in ether shaken with  $Ag_2CO_3$  (1 mole) gives (35% yield (114)) di-*ter*-butyl ether, b.p.  $106.5-107^\circ$ ,  $D_4^{20} = 0.7658$ ,  $n_D^{20} = 1.3949$  (114).]

$\bar{C}$  in the presence of small amts.  $AlCl_3$  exchanges halogen with reactive H atoms of certain hydrocarbons; e.g.,  $\bar{C}$  with 2,3-dimethylbutane (1:8515) +  $AlCl_3$  shaken for  $\frac{1}{2}$  min. at room temp. gives (23% yield (112)) 2-chloro-2,3-dimethylbutane (3:7600);  $\bar{C}$  with 2,2,3-trimethylbutane (1:8544) +  $AlCl_3$  shaken for 30-45 seconds gives (16% yield (112)) 3-chloro-2,2,3-trimethylbutane (3:4020); for other examples see (112).]

$\bar{C}$  also undergoes alcoholysis; e.g.,  $\bar{C}$  shaken with equal vol. 50 mole % MeOH for several days (74) (11) seps. a non-aq. phase of *ter*-butyl methyl ether (1:7830), b.p. 55°;  $\bar{C}$  with EtOH gives (11) *ter*-butyl ethyl ether (1:7860), b.p. 73°; for study of this equilibrium and deto. of these ethers see (11).]

[For rate of reactn. of  $\bar{C}$  with KI in acetone at 60° see (80); for reactn. of  $\bar{C}$  with Ca formate yielding (77) (78) *ter*-butyl formate (1:3033), b.p. 83°, see iodic. refs.; for conv. of  $\bar{C}$  to esters by htg. with alkali salt of a suitable acid under press. at 125-225° in pres. of Cu and the use of this reactn. in sepn. of  $\bar{C}$  from less reactive chlorine cpds. see (81).]

$\bar{C}$  readily condenses with arom. hydrocarbons and phenols; e.g.,  $\bar{C}$  with  $Al/Hg + C_6H_6$  gives (74 5% yield (109)) or  $\bar{C}$  with  $C_6H_6 + AlCl_3$  gives (yields: 69% (82), 60% (83)) (62) (1) mainly *ter*-butylbenzene (1:7460), b.p. 168.8°, often accompanied by some *p*-(di-*ter*-butyl)benzene, cryst. from alc., m.p. 77° (82); this same condensation can also be effected in anhydrous HCl at 235° under press. (88% yield (84)) or in anhydrous HF (yield: 60% di- + 10% mono- (85)). —  $\bar{C}$  with toluene +  $AlCl_3$  gives both *p*-*ter*-butyltoluene and *m*-*ter*-butyltoluene (in ratio of 30-35/65-70, resp. (85)) but  $\bar{C}$  with toluene in anhyd. HCl or HF (85) (22) cf. (113) gives exclusively (84) *p*-*ter*-butyltoluene, b.p. 188-189°,  $n_D^{20} = 1.4930$  (84). — For reactn. of  $\bar{C}$  with naphthalene +  $AlCl_3$  (87) or  $Al/Hg$  (109) or  $\bar{C}$  with *m*-cymene +  $AlCl_3$  (88) see iodic. refs.]

$\bar{C}$  with phenol (1:1420) in anhyd. HF gives (85% yield (89)) *p*-*ter*-butylphenol (1:1510);  $\bar{C}$  with  $\beta$ -naphthol (1:1540) +  $AlCl_3$  gives (90) 4-(*ter*-butyl)naphthol-2, m.p. 102° (90). —  $\bar{C}$  with anisole (1:7445) +  $ZnF_2$  gives (30 6% yield (91)) *p*-*ter*-butylanisole, but  $\bar{C}$  does not react with anisole +  $AlF_3$  or with furan +  $ZnF_2$  (91)]

$\bar{C}$  with acetanilide +  $AlCl_3$  in ethylene dichloride at -10° gives (93% yield) *N*-acetyl-*p*-*ter*-butylaniline (111).]

$\bar{C}$  under proper conditions gives the corresponding  $RMgCl$  cpd.: e.g.,  $\bar{C}$  with Mg in dry ether as directed gives (yields: 80% (92), 62% (93), 60% (95)) cf. (94) *ter*-BuMgCl; this  $RMgCl$  cpd. undergoes the usual reactions (see also below under @'s) including the following: *ter*-BuMgCl with  $O_2$  below 0° gives (80% yield (95)) *ter*-BuOH (1:6140) q.v.; with acetyl chloride (1 mole) in  $C_6H_6$  gives (40-54% yield (92)) *ter*-butyl methyl ketone (pinacolone) (1:5425) (note, however, that *ter*-BuMgCl with excess acetyl chloride takes a different course (97) and that with various other acyl halides the reducing action of the *ter*-BuMgCl becomes conspicuous cf. (98) (99) (100));  $\bar{C}$  with ethyl chloroformate (3:7295) or diethyl carbonate (1:3150) gives (56% yield (92)) ethyl trimethylacetate (ethyl pivalate) (1:3117), with  $\bar{C}$  itself to give (10% yield (96)) hexamethylethane (1:7090).

$\bar{C}$  reacts with other  $RMgX$  cpds. in conventional fashion; e.g.,  $\bar{C}$  with  $MeMgCl$  gives (42-50% yield (108)) tetramethylmethane (neopentane) (1:8499);  $\bar{C}$  with *n*-PrMgBr in ether +  $HgCl_2$  gives (yield 21% (101), 20% (110)) 2,2-dimethylpentane (1:8543); the numerous other reactions of *ter*-BuMgCl cannot be reviewed here.

[For reactn. of  $\bar{C}$  with  $Et_2Zn$  and numerous homologs see (102).]

Ⓐ *ter*-Butyl alcohol (1:6140): m.p. 25.6°, b.p. 82.5°. [From  $\bar{C}$  by shaking with aq. for 24 hrs. at room temp. (6), or on refluxing with 2 vols. aq. for 8 hrs. (72), neutralizing with  $Na_2CO_3$ , salting out the alcohol with NaCl, drying over anhyd.  $Na_2CO_3$ , and distilling.]

Ⓑ Trimethylacetic acid (pivalic acid) (1:0410): m.p. 35.5°, b.p. 163-164°. [From  $\bar{C}$  by

conversion to *ter*-BuMgCl (see above) and reactn. of latter with dry CO<sub>2</sub> (yields based on  $\bar{C}$ , 75% (92), 62% (93), 42.5% (17)) (94).]

⑤ Trimethylacetic anilide (pivalanilide): m.p. 132–133° u.c. (103), 132.5–133° (17). [From  $\bar{C}$  by conv. to *ter*-BuMgCl (see above) and reactn. of latter with phenyl isocyanate in dry ether (17) (103) (104).]

⑥ Trimethylaceto-*p*-toluidide (pivalo-*p*-tolnide): m.p. 119–120° u.c. (103). [From  $\bar{C}$  by conversion to *ter*-BuMgCl (see above) and reactn. of latter with *p*-tolyl isocyanate in dry ether (103).]

⑦ Trimethylaceto- $\alpha$ -naphthalide (pivalo- $\alpha$ -naphthalide): m.p. 146–147° u.c. (103) [From  $\bar{C}$  by conversion to *ter*-BuMgCl (see above) and reactn. of latter with  $\alpha$ -naphthyl isocyanate in dry ether (103).]

— *ter*-Butyl mercuric chloride: long ndls. from aq. acetone as directed (105), m.p. 122–123° dec. (105). [From *ter*-BuMgCl with HgCl<sub>2</sub> (105).]

— *S-ter*-Butylisothiourca picrate: m.p. 160–161° (106). [From  $\bar{C}$  with thiourea on htg. in alc. followed by conversion of the resultant hydrochloride to picrate (106); note, however, that, because of the lability of the *ter*-butyl radical, reactions carried out in MeOH or EtOH may give the corresp. *S*-methylisothiourca picrate, m.p. 224°, or *S*-ethylisothiourca picrate, m.p. 188°, and this definitely occurs (107) starting with *ter*-butyl iodide.]

— *N-(ter-Butyl)phthalimide*: unreported.

— *ter*-Butyl 2,4,6-triliodophenyl ether: unreported.

— *ter*-Butyl  $\alpha$ -naphthyl ether: unreported.

— *ter*-Butyl  $\beta$ -naphthyl ether: unreported.

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3:7065 ACETYL CHLORIDE  
(Ethanoyl chlorido)Beil. II - 173  
II<sub>1</sub>-(70)  
II<sub>2</sub>-(175)

## B.P.

## F.P.

55°	at 760 mm.	(1)	-112.0° (0)	$D_4^{25} = 1.0983$	(5)
51-52°	at 761 mm.	(2)		1.0982	(11)
52°	at 737 mm.	(3)			
51-52°		(12)		$D_4^{20.8} = 1.1037$	(12)
51-52°	at 720 mm.	(4)			
51.8°		(5)		$D_4^{20} = 1.1044$	(8)
51.0°	at 760 mm.	(6)		$n_D^{25} = 1.3878$	(5)
50.92°	at 746 mm.	(7)			
50.6°	at 756 mm.	(8)		$n_D^{20.8} = 1.38831$	(12)
50.2°		(9)			
50.08-50.12°	at 741 mm.	(10)		$n_D^{20} = 1.38076$	(4)
50°	at 740 mm.	(13)		1.3887	(8)

Colorless mobile liq. with sharp and penetrating odor. — Note that ordinary samples of  $\bar{C}$  may (according to their method of preparation) contain more or less  $\text{PCl}_3$  (b.p. 75.95° at 760 mm.),  $\text{POCl}_3$  (b.p. 107.2° at 760 mm.),  $\text{SOCl}_2$  (b.p. 78.8°),  $\text{AcOH}$  (b.p. 118.2°),  $\text{Ac}_2\text{O}$  (b.p. 140.0°), or various acetylated derivs. of phosphorous acid (if present in large amt. the last in part form a white ppt. on long stdg.), removal of which is difficult; the presence of these impurities doubtless accounts for various instances of abnormally high b.p.'s cf. (7). —  $\bar{C}$  may be freed from dissolved  $\text{HCl}$  and from  $\text{AcOH}$  by distn. with dimethylaniline (13) or by treatment with powdered basic oxides, hydroxides, carbonates, etc. (14).

PREPARATION OF  $\bar{C}$ 

$\bar{C}$  can be prepared from various sources with a wide variety of reagents; examples of the more important types of combinations are given below grouped under indicated subheadings. — It must also be recognized that many other processes (notably for manufacture of  $\text{Ac}_2\text{O}$ ) involve the formation of  $\bar{C}$  but immediately utilize it without separate isolation; these cannot be included here.

Preparation of  $\bar{C}$  from  $\text{AcOH}$ . [For prepn. of  $\bar{C}$  from  $\text{AcOH}$  with  $\text{PCl}_3$  (79% yield (20)) (15) (16) (7) (17) under press. at 80° (yield 100% (18)) or in  $\text{Ac}_2\text{O}$  (85% yield (19)) see indic. refs. (note particularly the formn. of  $\text{Ac}_2\text{O}$  and of  $\text{AcO.P(OH)}_2$  discussed in (17)): with  $\text{PCl}_3 + \text{ZnCl}_2$  (90% yield) see (20); with  $\text{PCl}_5$  (80% yield (20)) (21) see indic. refs.; with  $\text{POCl}_3$  (22) (23) see indic. refs.; with  $\text{P}_2\text{O}_5 + \text{HCl}$  gas at 0° see (24) (25); with  $\text{P} + \text{Cl}_2$  in  $\text{POCl}_3$  see (26).]

[For prepn. of  $\bar{C}$  from  $\text{AcOH}$  with  $\text{SOCl}_2$  (46% yield (20)), with  $\text{S}_2\text{Cl}_2 + \text{Cl}_2$  at -4° in pres. of  $\text{Fe}$  (95.5% yield (27)), with  $\text{ClSO}_3\text{H}$  (20-25% yield (28)); with sodium chlorosulfonate (29) in pres. of  $\text{NaCl}$  or  $\text{Na}_2\text{S}_2\text{O}_7$  (30) (31), or with  $\text{SiCl}_4$  in toluene (85% yield (32)), see indic. refs.]

[For prepn. of  $\bar{C}$  from  $\text{AcOH}$  with  $\text{COCl}_2$  (3:5000) at 110-120° (33) in vapor phase at 160° over  $\text{MgCl}_2$  on diatomaceous earth (34) cf. (35) (36); with an arylsulfochloride such as *p*-toluenesulfonyl chloride +  $\text{NaCl}$  (30); with another org. acid chloride such as chloroacetyl chloride (3:5235) (37), dichloroacetyl chloride (3:5290) (38), or benzoyl chloride (3:6240) (yield 85-88% (39), 70% (42)) (40) (41); with benzotrichloride (3:6540) (90% yield (42)) see indic. refs.]

Preparation of  $\bar{C}$  from salts of acetic acid. [For prepn. of  $\bar{C}$  from  $\text{NaOAc}$  (or other metallic acetates) with  $\text{POCl}_3$  (43) (44); with  $\text{SO}_2\text{Cl}_2$  (45) (46); with sodium chlorosulfonate

(29) cf. (30); with  $\text{SiCl}_4$  (47) (48); with  $\text{COCl}_2$  at  $120^\circ$  under press. (49); with *p*-toluene-sulfonyl chloride (50); with benzoyl chloride (3:6240) (40) see indic. refs.; from  $\text{NaOAc}/\text{H}_2\text{SO}_3$  compd. with  $\text{Cl}_2$  see (51).]

Preparation of  $\bar{\text{C}}$  from acetic anhydride. [For prepn. of  $\bar{\text{C}}$  from  $\text{Ac}_2\text{O}$  (1:1015) with  $\text{Cl}_2$  (52); with dry  $\text{HCl}$  gas at  $100^\circ$  (52) or in continuous process at  $85\text{--}90^\circ$  (93% yield (53)) or under 18–42 atm. press. (100% yield (54)); with  $\text{PCl}_3$  (15); with  $\text{PCl}_5$  (21); with  $\text{SOCl}_2$  at  $20\text{--}25^\circ$  ( $\text{SO}_2$  being evolved) (55), or with sodium chlorosulfonate (29) see indic. refs.]

[For prepn. of  $\bar{\text{C}}$  from  $\text{Ac}_2\text{O}$  (1:1015) with phosgene (3:5000) + cat. (56); with benzoyl chloride (3:6240) (77% yield (42)) (41) (40); with *nx*alyl (di)chloride (3:5060) (80–95% yield (57)); with benzo-trichloride (3:6540) +  $\text{ZnCl}_2$  (33% yield (58)); with benzyl chloride (3:8535) + cat. (59) see indic. refs.; for formn. of  $\bar{\text{C}}$  as by-prod. from reactn. of ethylene with  $\text{Cl}_2$  in  $\text{Ac}_2\text{O}$  see (60).]

Preparation of  $\bar{\text{C}}$  from methyl chloride. [For prepn. of  $\bar{\text{C}}$  from  $\text{CH}_3\text{Cl}$  (3:7005) with  $\text{CO}$  at  $700\text{--}800^\circ$  over pumice contg. sodium metaphosphate (61) or with  $\text{CO}$ ,  $\text{COCl}_2$ , or  $\text{COS}$  at  $700\text{--}900^\circ$  in pres. of metallic cat. (62) see indic. refs.]

Preparation of  $\bar{\text{C}}$  from miscellaneous sources. [For prepn. of  $\bar{\text{C}}$  from 1,1,1-trichloroethane (methylchloroform) (3:5085) by partial cat. hydrolysis (63) (64); from ketene + liq.  $\text{HCl}$  (65) or with  $\text{HCl}$  gas over activated carbon at  $100^\circ$  (100% yield (66)); from ethyl, isobutyl, isoamyl, benzyl, phenyl, or *p*-tolyl acetates with  $\text{SiCl}_4$  (67); from  $\alpha$ -chloroethyl acetate (3:7625) (68) (69) or  $\alpha,\beta$ -dichloroethyl acetate (69) with  $\text{ZnCl}_2$  (68) or over pumice at  $250\text{--}300^\circ$  (69); from  $\beta$ -bromo- $\alpha,\beta$ -dichlorovinyl ethyl ether with  $\text{AcOH}$  (70); from acetyl bromide with  $\text{HCl}$  gas at ord. temp. (71); from *N,N*-diacetylaniline (diacetanilide) with  $\text{HCl}$  gas at  $150\text{--}170^\circ$  (72); from diacetyl sulfite (see below) with  $\text{SOCl}_2$  (73) see indic. refs.]

### PYROLYSIS OF $\bar{\text{C}}$

[ $\bar{\text{C}}$  in absence of cat. is stable to heat up to at least  $450^\circ$  (74). —  $\bar{\text{C}}$  passed at  $700\text{--}850^\circ$  over hot Pt wire gives ethylene +  $\text{CO}$  +  $\text{HCl}$  (75), but at  $400^\circ$  over Pt on pumice gives (74) 45%  $\text{MeCl}$  (3:7005) + 49%  $\text{CO}$  + 5%  $\text{H}_2$ . —  $\bar{\text{C}}$  over Cu filings at  $350^\circ$  is partially decomposed yielding (74)  $\text{MeCl}$  (3:7005) +  $\text{CO}$  +  $\text{CO}_2$  +  $\text{H}_2$  + dehydroacetic acid (1:0700) + acetone. —  $\bar{\text{C}}$  over  $\text{ZnCl}_2$  on pumice at  $400^\circ$  gives (74)  $\text{HCl}$  + dehydroacetic acid (1:0700) + gas mixt. contg. 87%  $\text{CO}_2$  + 4%  $\text{CO}$  + 2%  $\text{H}_2$ . —  $\bar{\text{C}}$  over Ni at  $420^\circ$  gives (76)  $\text{HCl}$  + gas mixt. contg. 62%  $\text{CO}$  + 32%  $\text{H}_2$ . — For studies on pyrolysis of  $\bar{\text{C}}$  over  $\text{Al}_2\text{O}_3$ ,  $\text{Cu}_2\text{Cl}_2$ ,  $\text{CuO}$ , Ni, etc., see (74).]

### REACTIONS OF $\bar{\text{C}}$ WITH INORGANIC REAGENTS

Reaction of  $\bar{\text{C}}$  with  $\text{H}_2\text{O}$  (hydrolysis).  $\bar{\text{C}}$  reacts violently with aq. hydrolyzing to  $\text{AcOH}$  (1:1010) +  $\text{HCl}$  (for kinetic studies see (77)); for use of this reactn. in volumetric detn. of  $\text{H}_2\text{O}$  in org. liquids see (185) (78). — Because of its ease of reactn. with aq.  $\bar{\text{C}}$  is widely used for condensations, ring closures, etc.

Reaction of  $\bar{\text{C}}$  with  $\text{NH}_3$  and similar cpds.  $\bar{\text{C}}$  with cold conc. aq.  $\text{NH}_4\text{OH}$  (16) or  $\bar{\text{C}}$  with liq.  $\text{NH}_3$  (79) gives (yields: 77% (16), 88% (79)) acetamide, very sol. aq., m.p.  $81.5^\circ$ , b.p.  $222^\circ$  (best recrystd. from dry  $\text{AcOEt}$  by addn. of dry ether).

[The direct reaction of  $\bar{\text{C}}$  with  $\text{NH}_2\text{OH}$  (or its salts) seems to be unreported, but the presumable prod., viz., *N*-acetylhydroxylamine (acethydroxamic acid) [Beil. II-187, II<sub>2</sub>-(85), II<sub>2</sub>-(181)], very eas. sol. aq. or alc., insol. ether, cryst. from  $\text{EtOAc}$ , m.p. anhydrous  $89^\circ$ , contg. crystal aq.  $57^\circ$ , has been obtd. indirectly.]

[The direct reactn. of  $\bar{\text{C}}$  with hydrazine hydrate,  $\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}$ , seems to be unreported, but the presumable prod., viz., acethydrazide (acetylhydrazine) [Beil. II-191, II<sub>2</sub>-(86), II<sub>2</sub>-(185)], ndls. from alc., m.p.  $67^\circ$ , has been obtd. by indirect means.]

Reaction of  $\bar{C}$  with halogens. [ $\bar{C}$  with  $Cl_2$  in  $CCl_4$  in light (80) or in pres. of  $I_2$  (82) gives mainly chloroacetyl chloride (3:5235); for study of mechanism of chlorination see (81); for influence of  $\bar{C}$  on chlorination of  $AcOH$  or  $Ac_2O$  see (82), on bromination of  $AcOH$  see (83).]

[For studies of  $\bar{C}$  with  $Br_2$  see (84) (85) (86).]

Reaction of  $\bar{C}$  with inorganic acids. [ $\bar{C}$  with dry  $HBr$  gas for 2 hrs. gives (80% yield (87)) acetyl bromide [Beil. II-174, II<sub>1</sub>-(79), II<sub>2</sub>-(176)], b.p. 76.7° at 760 mm.,  $D_4^{15.8} = 1.6625$ ,  $n_D^{15.8} = 1.45370$ ; for details on this equilibrium see (88).]

[ $\bar{C}$  with 3 pts. dry  $HI$  in the cold gives (70% yield (87)) (89) acetyl iodide [Beil. II-174, II<sub>1</sub>-(80), II<sub>2</sub>-(177)], h.p. 104–106° at 735 mm. (89) (for studies of use of  $AcI$  in splitting of aliphatic ethers (90) or in addn. to unsatd. hydrocarbons (91) see indic. refs.).]

[ $\bar{C}$  with cold conc.  $H_2SO_4$  (1 mole) forms a mol. cpd. (88) (92) which can even be obt'd. in cryst. form (92); this cpd. loses  $HCl$  only upon htg. (88) (92), and the residual acetyl hydrogen sulfate [Beil. II-170, II<sub>1</sub>-(78), II<sub>2</sub>-(174)] which might be expected is transformed into sulfoacetic acid and other prods. (92). —  $\bar{C}$  with nitrosylsulfuric acid in  $CCl_4$  evolves  $NOCl$  and yields acetyl  $HSO_4$  which rapidly changes to sulfoacetic acid (93).]

[ $\bar{C}$  with  $ClSO_3H$  stood for several days (94) (95) evolves  $HCl$  and forms the transient acetyl sulfonyl chloride,  $CH_3CO.O.SO_2Cl$ ; above 45° this intermediate rearr. to sulfoacetyl chlorido which with water hydrolyzes to sulfoacetic acid;  $\bar{C}$  with  $ClCO_2H$  at 60–140°, however, also undergoes condensation involving 4 moles of  $\bar{C}$  with evoln. of  $HCl$  and formn. of an acid chloride which on hydrolysis with aq. gives (3% yield (94)) a monobasic acid of compn.  $C_8H_5O_4$  [Beil. XVIII-412], m.p. 99°, which is either 2,6-dimethylpyrone-4-carboxylic acid-3 or 2-methylpyrone-1,4-acetic acid-6 (96); note that this acid is isomeric with but distinct from dehydroacetic acid (1:0700), m.p. 109°. — Note also that  $\bar{C}$  in  $AcOH$  boiled with conc.  $H_2SO_4$  gives (97) traces of 2,6-dimethylpyrone.]

[ $\bar{C}$  with solid  $H_2O_2$  (0.6 mole) yields (98) about 60% acetyl hydrogen peroxide (peracetic acid) [Beil. II-109, II<sub>1</sub>-(78), II<sub>2</sub>-(174)] accompanied by some diacetyl peroxide [Beil. II-170, II<sub>1</sub>-(78), II<sub>2</sub>-(174)]. —  $\bar{C}$  with liq.  $H_2S$  yields (99) "dithioacetic acid anhydride,"  $(CH_3CS)_2S$ , white cryst., m.p. 225° (99); note that, although neither  $\bar{C}$  nor  $Ac_2O$  separately treated with  $H_2S$  gas shows any appreciable reaction, yet  $Ac_2O$  contg. 2%  $\bar{C}$  absorbs  $H_2S$  giving (70% yield (100)) thiolacetic acid [Beil. II-230, II<sub>1</sub>-(101), II<sub>2</sub>-(208)],  $CH_3CO.SH$ , b.p. 93°. —  $\bar{C}$  (4 moles) with  $H_2S_3 + ZnCl_2$  yields (101) diacetyl trisulfide.]

Reaction of  $\bar{C}$  with salts of inorganic acids. [ $\bar{C}$  with metal oxides in  $CHCl_3$  at –60 to –20° yields (102) the corresp. metallic chlorides. —  $\bar{C}$  with  $Sb_2S_3$  at 300–350° (103) or with  $K_2S$  (104) gives diacetyl sulfide [Beil. II-232], b.p. 120°. —  $\bar{C}$  with  $PbSO_3$  gives (72) diacetyl sulfite which with  $SOCl_2$  gives  $\bar{C} + SO_2$  (72).]

[ $\bar{C}$  (6 pts.) with  $KNO_3$  (first fused, then powdered) (1 pt.) (105) or  $\bar{C}$  with  $Pb(NO_3)_2$  (106) gives mainly (yields: 81–85% (105), 58% (106)) acetic anhydride (1:1015).]

[ $\bar{C}$  with  $NaN_3$  in di-isomyl ether stood overnight (108) (109), then warmed at 60–70°, evolves  $N_2$  and gives (86% yield (107)) methyl isocyanate [Beil. IV-77, IV<sub>1</sub>-(337), IV<sub>2</sub>-(578)], b.p. 27.4–27.8°; note, however, that  $\bar{C}$  with  $NaN_3$  in  $AcOH$  evolves  $N_2$  and gives (50–63% yield (110)) *N*-methylacetamide, m.p. 27–28°, b.p. 202–204° (presumably by cleavage of the  $CH_3NCO$  and acetylation of the  $MeNH_2$ ).]

[ $\bar{C}$  with  $NaHF_2$  in  $Ac_2O$  (111), with  $KF$  in  $AcOH$  (41) (42),  $AgF$  (112),  $ZnF_2$  (112) (113),  $HgF_2$  (114),  $C_6H_5HgF$  (115),  $SbF_3$  (112) (116), or  $AsF_3$  (112) gives (yields: 132% on  $\bar{C}$  or 66% on  $NaHF_2$  (111), 76% (41) (42), 40% (113), 30.8% (116)) acetyl fluoride, b.p. 20.8° at 770 mm.]

[ $\bar{C}$  with  $AlCl_3$  in  $CS_2$  at –10° gives (117) a mol. cpd.,  $\bar{C}.AlCl_3$ , as a pale yel. gummy mass;  $\bar{C}$  with  $AlCl_3.Et_2O$  gives  $EtOAc$  (70% yield (118)) +  $EtCl$  (3:7015) +  $AlCl_3$ . —  $\bar{C}$  (1 mole) with  $AlCl_3$  (6 moles) in  $CHCl_3$  gives (124)  $(CH_3CO)_2CH.CCl_2.O.AlCl_2$  (125) which with

aq. yields (124) (125) acetylacetone (1:1700). — Note also that  $\bar{C}$  forms other analogous complexes. e.g.,  $\bar{C} \cdot \text{BCl}_3$  (119),  $\bar{C} \cdot \text{BF}_3$  (119),  $\bar{C} \cdot \text{SbCl}_5$  (119) (for use of these in splitting of ethers see (119)).]

[ $\bar{C}$  with 2 pts. sublimed  $\text{FeCl}_3$  in  $\text{CS}_2$  for 24 hrs. gives (small yield (120)) dehydroacetic acid (1:0700).]

[ $\bar{C}$  with  $\text{CaI}_2$  in s.t. at 70–75° for 120 hrs. gives (121) acetyl iodide (see above under H1).]

Reaction of  $\bar{C}$  with esters of inorganic acids. [ $\bar{C}$  with  $\text{Me}_2\text{SO}_4$  (1 mole) + trace of  $\text{ZnCl}_2$  at 140–150° evolves  $\text{HCl}$  and gives (20–25% yield (122)) dimethyl sulfoacetate, b.p. 155–165° nt 20–22 mm. (122). —  $\bar{C}$  + di-*n*-propyl sulfite + trace  $\text{ZnCl}_2$  at 170–200° gives (80% yield (123)) *n*-propyl acetate (1:3075).]

Reaction of  $\bar{C}$  with metals. [ $\bar{C}$  in excess with metallic  $\text{Zn}$  gives a solid of compn.  $\text{C}_{14}\text{H}_{18}\text{O}_4$  (126), now (127) thought to be 3,8-diacetyl-5,6-dimethyldecatetraene-3,4,6,7-dione-2,9. —  $\bar{C}$  with metallic  $\text{Zn}$  in dry ether yields (128)  $\text{EtOAc}$  (1:3015) and  $\text{AcOH}$  (1:1010). —  $\bar{C}$  with metallic  $\text{Zn}$  in dry dioxane (1:6400) gives (85% yield (128)) (129) ethylene glycol diacetate (1:3511). —  $\bar{C}$  with  $\text{CuH}$  evolves  $\text{H}_2$  and gives (130) cf. (131)  $\text{EtOAc}$  (1:3015) + ethylidene diacetate (1:3383).]

## REACTIONS OF $\bar{C}$ WITH ORGANIC REAGENTS

### REACTIONS OF $\bar{C}$ WITH HYDROCARBONS

Reactions of  $\bar{C}$  with alkanes. [ $\bar{C}$  with *n*-butane (or isobutane) +  $\text{AlCl}_3$  at 60° for 15 hrs. under press. gives (small yield (132)) isobutyl methyl ketone (1:5430) —  $\bar{C}$  with *n*-pentane +  $\text{AlCl}_3$  at 15° at ord. press. gives (10% yield (133)) (134) 2,3-dimethylpentanone-4 (*unsym*-isopropyl-methyl-acetone) [Beil. I-703, I<sub>1</sub>-(360)], b.p. 135–136° (oxime, b.p. 101–105° at 20 mm., semicarbazone, m.p. 114° (133)) accompanied (134) by some 2,3-dimethylpenten-3-one-2 (*unsym*-isopropylidene-methyl-acetone) [Beil. I<sub>2</sub>-(798)] (corresp. semicarbazone, m.p. 192.5° (134)). —  $\bar{C}$  with *n*-hexane +  $\text{AlCl}_3$  in similar fashion gives (7% yield (135)) (134) 3-ethyl-2-methylpentanone-4 (*unsym*-ethyl-isopropyl-acetone) [Beil. I-707], b.p. 154–155° (semicarbazone, m.p. 120° (135)) accompanied by a little 3-ethyl-2-methylpenten-2-one-4 (*unsym*-ethyl-isopropylidene-acetone), b.p. 177–178° (semicarbazone, m.p. 220° (135)).]

Reactions of  $\bar{C}$  with alkenes. [ $\bar{C}$  in the pres. of suitable cat. can add to olefin linkages forming halogenated ketones: e.g.,  $\bar{C}$  with ethylene +  $\text{AlCl}_3$  at 0° (137) (138) or  $\bar{C}$  + ethylene over activated carbon at 100° and 50 atm. (139) gives (yields: 53% (136), 33% (137)) (138) cf. (60)  $\beta$ -chloroethyl methyl ketone (3:7640) (note that  $\bar{C}$  + ethylene +  $\text{AlCl}_3$  in  $\text{CS}_2$ , latter subsequently replaced by  $\text{C}_6\text{H}_6$ , goes further yielding (140) benzylacetone [Beil. VII-314, VII<sub>1</sub>-(167)], b.p. 235°). — For studies of analogous cat. addn. of  $\bar{C}$  to 2-methylbutene-2, 2,3-dimethylbutene-2, and 2-methylhexene-2 see (141).]

Reactions of  $\bar{C}$  with alkynes. [ $\bar{C}$  in the pres. of suitable cat. can also add to a triple unsatd linkage yielding olefinic chloroketones: e.g.,  $\bar{C}$  with acetylene +  $\text{AlCl}_3$  at 15° (142) (143) or other cat. (143) gives (25% yield (142))  $\beta$ -chlorovinyl methyl ketone, b.p. 35–38° at 12 mm. (143). —  $\bar{C}$  with butyne-1 (ethylacetylene) +  $\text{SnCl}_4$  gives (144) 4-chlorohexen-3-one-2, b.p. 46–53° at 10 mm.,  $D_4^{25} = 1.0973$ ,  $n_D^{25} = 1.4906$  (144); for analogous reactions with pentyne-1, hexyne-1, hexyne-3, heptyne-1, octyne-4, decyne-5, and dodecyne-6 together with corresp. constants of prods. see (144).]

Reaction of  $\bar{C}$  with cycloparaffins (cycloalkanes). [ $\bar{C}$  in the pres. of  $\text{AlCl}_3$  also condenses with cycloalkanes eliminating  $\text{HCl}$ ; e.g.,  $\bar{C}$  (1.9 moles) + cyclopentane (1:8400) (5.4 moles) +  $\text{AlCl}_3$  (2.2 moles) at 0° gives (145) cyclopentyl methyl ketone (acetylcyclopentane), b.p. 159.5–160.5° at 760 mm.,  $D_{20}^{20} = 0.9172$ ,  $n = \frac{20}{D} 1.44351$  (145) (semicarbazone, m.p. 142–143° (145));  $\bar{C}$  + methylcyclopentane (1:8403) +  $\text{AlCl}_3$  similarly gives (145) 1-

methylcyclopentyl-2 methyl ketone (1-acetyl-2-methylcyclopentane) accompanied by some 1-methylcyclopenten-1-yl-2 methyl ketone (1-acetyl-2-methylcyclopentene-1) (see below).]

[ $\bar{C}$  in the pres. of  $AlCl_3$  also condenses with cyclohexane, but here the reaction involves in addn. a change from a 6-membered to 5-membered ring: e.g.,  $\bar{C}$  with cyclohexane (1:8405) +  $AlCl_3$  gives (135) (146) (147) (148) 1-methylcyclopentyl-2 methyl ketone (1-acetyl-2-methylcyclopentane), b.p. 167-168° at 759 mm.,  $D_4^{20} = 0.8976$ ,  $n_D^{20} = 1.4404$  (semicarbazone, m.p. 162.5-163° (148), 158° (146)); *p*-nitrophenylhydrazine, m.p. 102.5° (148)), accompanied under certain circumstances (135) by 1-methylcyclopenten-1-yl-2 methyl ketone (1-acetyl-2-methylcyclopentene-1), b.p. 185-187° (135) (oxime, m.p. 85-85.5° (148), *p*-nitrophenylhydrazone, m.p. 162° (148), semicarbazone, m.p. 221° (148), 220° (133)); note that various hydrocarbon by-products are also formed. —  $\bar{C}$  + methylcyclohexane (hexahydrotoluene) (1:8410) +  $AlCl_3$  at room temp. similarly gives (149) 1-acetyl-2,3-dimethylcyclopentane, b.p. 182-184° at 754 mm.,  $D_4^{20} = 0.8969$ ,  $n_D^{20} = 1.44551$  (semicarbazone, m.p. 152°) (149).]

Reaction of  $\bar{C}$  with cycloalkenes. [ $\bar{C}$  in the pres. of suitable cat. adds to unsatd. linkages of cycloalkenes: e.g.,  $\bar{C}$  with cyclopentene (1:8037) +  $AlCl_3$  (2 moles) in cyclohexane at -15° gives (50% yield (150)) cyclopentyl methyl ketone (1-acetylcyclopentane) (for constants see above under  $\bar{C}$  + cyclopentane); note, however, that  $\bar{C}$  + cyclopentene (1:8037) +  $AlCl_3$  at -14° in  $CS_2$  (the latter being subsequently replaced by benzene) gives (140) 1-acetyl-3-phenylcyclopentane (note rearr.).]

[ $\bar{C}$  with cyclohexene (1:8070) +  $AlCl_3$  (2 moles) in cyclohexane gives (53% yield (150)) cyclohexyl methyl ketone (1-acetylcyclohexane) [Beil. VII-22, VII-(16)]. —  $\bar{C}$  with cyclohexene (1:8070) +  $AlCl_3$  (1 mole) in  $CS_2$  gives (21% yield (151)) (152) cyclohexen-1-yl-1 methyl ketone (1-acetylcyclohexene-1) (tetrahydroacetophenone) [Beil. VII-58, VII-(49)], b.p. 201-202°,  $D_4^{20} = 0.9655$ ,  $n_D^{20} = 1.4881$  (oxime, m.p. 99°, semicarbazone, m.p. 220-221°). —  $\bar{C}$  with cyclohexene (1:8070) +  $AlCl_3$  in  $CS_2$  at -15° gives by addn. a prod. supposed (153) to be 2-chlorocyclohexyl-1 methyl ketone (since it can be converted by loss of HCl to tetrahydroacetophenone (above)) but which when reacted with  $C_6H_6$  +  $AlCl_3$  gives (140) 4-phenylcyclohexyl-1 methyl ketone (1-acetyl-4-phenylcyclohexane); in just which phase rearr. occurs has not been established with certainty.]

Reaction of  $\bar{C}$  with aromatic hydrocarbons.  $\bar{C}$  with aromatic hydrocarbons in the presence of various cat. (notably  $AlCl_3$ ) evolves HCl and yields aryl methyl ketones; examples are cited in the following paragraphs.

[ $\bar{C}$  with  $C_6H_6$  +  $AlCl_3$  (154) in  $CS_2$  (155) gives (70% yield (155)) methyl phenyl ketone (acetophenone) (1:5515) accompanied by a little 1,3-diphenylbuten-2-one-1 (dyphone) cf. (155); for study of relative reactivity in this sense of  $AcF$ ,  $AcCl$ ,  $AcBr$ , and  $AcI$  see (111); for study of influence of other cat., e.g.,  $FeCl_3$  (156) (157),  $TiCl_3$  (158),  $ZrCl_4$  (159),  $UCl_4$  (160),  $BeCl_2$  (161), Al powder (162) or Cr powder (163), or for study of effect of various solvents with  $AlCl_3$  (164) see indic. refs.]

[ $\bar{C}$  with toluene +  $AlCl_3$  gives (70% yield (165)) (166) methyl *p*-tolyl ketone (1:5530); for study of use of  $BeCl_2$  (80% yield (161)) or of 39 other metallic chlorides (167) (168) see indic. refs. — For reactn. of  $\bar{C}$  +  $AlCl_3$  with a long series of homologous monoalkylbenzenes see (169) (170), with *p*-cymene (1:7505) see (171); many other, similar cases cannot be included here.]

[ $\bar{C}$  with naphthalene (1:7200) +  $AlCl_3$  in  $CS_2$  gives a mixt. (75% yield (172)) comprising 50-60% 1-acetylnaphthalene (1:5600) + 15-20% 2-acetylnaphthalene (1:5153). —  $\bar{C}$  with 1-methylnaphthalene (1:7600) +  $AlCl_3$  in nitrobenzene at -3° gives (173) cf. (174) 1-aceto-4-methylnaphthalene;  $\bar{C}$  with 2-methylnaphthalene (1:7605) +  $AlCl_3$  in nitrobenzene gives a mixt. (64% yield (175)) comprising mainly 6-acetyl-2-methylnaphthalene accompanied by some 8-acetyl-2-methylnaphthalene.]

[ $\bar{C}$  with biphenyl (1:7175) +  $AlCl_3$  in  $CS_2$  (176) or  $C_6H_6$  (177) gives (yields: 90% (176), 70% (177)) 4-acetylbiphenyl (*p*-phenylacetophenone) (1:5201); under appropriate conditions  $\bar{C}$  with biphenyl +  $AlCl_3$  in  $CS_2$  gives (yields: 45% (176), 43% (178)) 4,4'-diacetylbiphenyl.]

[ $\bar{C}$  with acenaphthene (1:7225) +  $AlCl_3$  in nitrobenzene (179) or with liq. HF (180) gives (20% yield (180)) 1-acetoacenaphthene.]

[Friedel-Crafts condensation can also be carried out with  $\bar{C}$  and heterocyclic systems: e.g.,  $\bar{C}$  with thiophene +  $SnCl_4$  in  $C_6H_6$  gives (79-83% yield (181)) 2-acetylthiophene (methyl 2-thienyl ketone),  $\bar{C}$  with thionaphthene +  $AlCl_3$  in  $CS_2$  gives (30% yield (182)) 3-acetylthionaphthene.]

### REACTIONS OF $\bar{C}$ WITH ORGANIC OH (OR SH) COMPOUNDS (OR THEIR METALLIC DERIVATIVES)

Reactions of  $\bar{C}$  with alcohols. [ $\bar{C}$  reacts with alcs. in general yielding the corresp. acetates: e.g.,  $\bar{C}$  with MeOH (1:6120) yields methyl acetate (1:3005),  $\bar{C}$  with EtOH (1:6130) yields EtOAc (1:3015), etc.; for studies on rate of reactn. of  $\bar{C}$  with EtOH in ether (1), or with  $\beta$ -chloroethyl alc. in dioxane (182) (183), or with benzyl alc. or cyclohexanol (182) see indic. refs.] — For use of  $\bar{C}$  in quant. detn. of OH groups in prim. and sec. alcs. see (186) (187) (188) cf. (185).

[Special interest, however, attaches to reaction of  $\bar{C}$  with *ter*-alcohols: under ord. conditions these react with  $\bar{C}$  to exchange Cl for OH yielding alkyl chloride + AcOH (e.g.,  $\bar{C}$  + *ter*-butyl alc. giving *ter*-BuCl + AcOH); note, therefore, that under special conditions  $\bar{C}$  with *ter*-alcs. also gives the corresp. esters; e.g.,  $\bar{C}$  with *ter*-butyl alc. (1:6140) in dry ether + Mg (189) (190) or dimethylaniline (191) or in xylene with pyridine (192) gives (yields: 98% (192), 83% (189), 63-68% (191), 45-55% (190)) *ter*-butyl acetate (1:3057); other *ter*-alcs. (189) and other acid chlorides (191) behave similarly.]

[For reactn. of  $\bar{C}$  with cellulose (or cotton) see (193) (194) (195); with polyoxymethylenes see (196).]

[ $\bar{C}$  with mercaptans yields the corresp. thiolacetates: e.g.,  $\bar{C}$  with  $C_2H_5SH$  gives (80% yield (197)) ethyl thiolacetate,  $CH_3CO.S C_2H_5$ , b.p. 116-117°,  $D_4^{25} = 0.0755$ ,  $n_D^{25} = 1.4503$  (197).]

Reactions of  $\bar{C}$  with phenols.  $\bar{C}$  can react with phenols in either or both of two modes: on one hand it can acetylate the phenolic OH yielding the corresp. phenol acetates, or in the pres. of suitable cat. or solvents it can condense with one or more of the nuclear H atoms yielding phenolic ketones. Furthermore the phenol acetates can more or less readily be caused to rearr. into phenolic ketones (Fries rearr.) so that the chemistry of the two classes is closely related and so voluminous that it cannot be given extensive discussion here.

[ $\bar{C}$  with phenol (1:1420) directly (198) (199) or in  $C_6H_6$  + Mg (200) gives (yields: 92% (200), 90% (199)) phenyl acetate (1:3571); other mono-, di-, and polyhydric phenols behave analogously.]

[ $\bar{C}$  with phenol (1:1420) +  $FeCl_3$  in  $CS_2$  (156) (201) or phenyl acetate (above) +  $AlCl_3$  in nitrobenzene at 20-25° for 24 hrs. (202) gives (yields: 75% (202), 33% (201)) *p*-hydroxyacetophenone (1:1527), m.p. 109° (for extensive review of the Fries rearr. reactn. see (203)); the corresp. analogous reactns. of  $\bar{C}$  with other mono-, di-, and polyhydric phenols are legion and will not be cited here.]

[For study of series of mol. cpds. of  $\bar{C}$  with various benzenesulphenols see (230).]

Reaction of  $\bar{C}$  with phenol ethers. With phenol ethers where no phenolic OH remains to interfere  $\bar{C}$  reacts in the pres. of suitable cat. in the Friedel-Crafts sense: e.g., [ $\bar{C}$  (2 moles) with methyl phenyl ether (anisole) (1:7445) (1 mole) +  $AlCl_3$  (2 moles) gives (75% yield

(204) (205) *p*-methoxyacetophenone (*p*-acetylanisole) (1:5140); note that  $\bar{C}$  + anisole do not react in the pres. of  $AlF_3$  or  $ZnF_2$  (111). — Countless analogous condensations of  $\bar{C}$  with other phenol ethers cannot be discussed here].

Reaction of  $\bar{C}$  with enols (or their metallic derivatives). [The reaction of  $\bar{C}$  with ethyl acetoacetate (1:1710) leads according to circumstances to either or both of two very closely similar derivatives; one of these is ethyl *O*-acetylacetoacetate (ethyl  $\beta$ -acetoxyacrylate) (A) [Beil. III-373, III<sub>1</sub>-(135), III<sub>2</sub>-(255)], b.p. 212–214° al. dec. (206),  $D_4^{20} = 1.060$  (207),  $n_D^{20} = 1.4447$  (207); the other is ethyl  $\alpha$ -acetylacetoacetate (ethyl diacetylacetate) (B) [Beil. III-751, III<sub>1</sub>-(263), III<sub>2</sub>-(467)], h.p. 209–211° (208),  $D_4^{20} = 1.093$  (207),  $n_D^{20} = 1.4687$  (207); note that the latter (B) as liquid is 100% enolized (209) (210) and this prop. is used (211) for detn. of both A + B in their mixtures. — Note furthermore that the *O*-ester (A) by suitable htg. (212) (213) (214) (215) (216) can be converted to the isomer (B).]

[ $\bar{C}$  with ethyl acetoacetate (1:1710) in pres. of pyridine (217) or  $\bar{C}$  with its Na enolate in ether (210) or its Cu enolate in ether or  $C_6H_6$  (220) gives mainly the *O*-acetyl deriv. (A) (above);  $\bar{C}$  with ethyl sodioacetoacetate in ether (221) (222) (223) (226) or pet. ether (216) or with the Ca enolate in  $C_6H_6$  (224) or  $\bar{C}$  with ethyl acetoacetate + Mg in  $C_6H_6$  (225) (226) gives (yields: 65% (224), 46–52% (225)) ethyl diacetylacetate (B above) (Cu enolate, m.p. 151° (220)).]

[For study of influence of  $\bar{C}$  on rate of enolization of ethyl acetoacetate see (228); for formn. of ethyl *O*-acetylacetoacetate (isomer A above) from  $\bar{C}$  + ketene diethylacetal (30% yield together with other prods.) see (229).]

Reaction of  $\bar{C}$  with acids or their salts. [ $\bar{C}$  on htg. with NaOAc or other metal salts of COOH yields acetic anhydride (1:1015); this reactn. is well known and will not be amplified here;  $\bar{C}$  with salts of acids other than acetic gives in some cases the corresp. mixed anhydride, others only the anhydride of the second acid. E.g.,  $\bar{C}$  (1 mole) with dry Na isovalerate (mole) gives at 120° the mixed anhydride contg. 1 acetyl and 1 isovaleroyl radical (231); the other hand,  $\bar{C}$  with dry Na cinnamate gives only cinnamic anhydride (231); many examples are known.]

[on htg. with AcOH under appropriate conditions (232) (233) (234) loses HCl giving yields  $Ac_2O$  (1:1016).]

to that  $\bar{C}$  in  $Ac_2O$  behaves as a weak acid and can actually be titrated with NaOAc.  $\bar{C}$  using methyl orange as indicator (235).

#### REACTION OF $\bar{C}$ WITH AMINES (OR THEIR DERIVATIVES)

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[Note also that  $\bar{\text{C}}$  with 2,4,6-trimethylbenzyl  $\text{MgBr}$  (mesityl  $\text{MgBr}$ ) gives (257) mesitylene but not 2,4,6-trimethylacetophenone (necetomesitylene) although  $\bar{\text{C}}$  with 2,4,6-triphenylphenyl  $\text{MgBr}$  does give (258) the corresp. 2,4,6-triphenylacetophenone.]

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[ $\bar{\text{C}}$  with  $\text{Et}_2\text{Mg}$  gives (261) 3-methylpentanol-3 (1:6189) (not *ter*-butyl alc. as was formerly supposed);  $\bar{\text{C}}$  with dibenzylzinc in pet. ether gives (262) 9% ketones;  $\bar{\text{C}}$  with dibenzylcadmium in ether gives (262) 18% phenylacetone (1:5118),  $\bar{\text{C}}$  with  $\text{Et}_2\text{Hg}$  gives



{204}) {205} *p*-methoxyacetophenone (*p*-acetylanisole) (1:5140); note that  $\bar{C}$  + anisole do not react in the pres. of  $AlF_3$  or  $ZnF_2$  (111). — Countless analogous condensations of  $\bar{C}$  with other phenol ethers cannot be discussed here].

Reaction of  $\bar{C}$  with enols (or their metallic derivatives). [The reaction of  $\bar{C}$  with ethyl acetoacetate (1:1710) leads according to circumstances to either or both of two very closely similar derivatives; one of these is ethyl *O*-acetylacetoacetate (ethyl  $\beta$ -acetoxyacrylate) (A) [Beil. III-373, III<sub>1</sub>-(135), III<sub>2</sub>-(255)], b.p. 212–214° sl. dec. (206),  $D_4^{20} = 1.060$  (207),  $n_D^{20} = 1.4447$  (207); the other is ethyl  $\alpha$ -acetylacetoacetate (ethyl diacetylacetate) (B) [Beil. III-751, III<sub>1</sub>-(263), III<sub>2</sub>-(467)], b.p. 209–211° (208),  $D_4^{20} = 1.093$  (207),  $n_D^{20} = 1.4687$  (207); note that the latter (B) as liquid is 100% enolized (209) (210) and this prop. is used (211) for detn. of both A + B in their mixtures. — Note furthermore that the *O*-ester (A) by suitable htg. (212) (213) (214) (215) (216) can be converted to the isomer (B).]

[ $\bar{C}$  with ethyl acetoacetate (1:1710) in pres. of pyridine (217) or  $\bar{C}$  with its Na enolate in ether (219) or its Cu enolate in ether or  $C_6H_6$  (220) gives mainly the *O*-acetyl deriv. (A) (above);  $\bar{C}$  with ethyl sodioacetoacetate in ether (221) (222) (223) (226) or pet. ether (216) or with the Ca enolate in  $C_6H_6$  (224) or  $\bar{C}$  with ethyl acetoacetate + Mg in  $C_6H_6$  (225) (226) gives (yields: 65% (224), 46–52% (225)) ethyl diacetylacetate (B above) (Cu enolate, m.p. 151° (226)).]

[For study of influence of  $\bar{C}$  on rate of enolization of ethyl acetoacetate see (228); for formn. of ethyl *O*-acetylacetoacetate (isomer A above) from  $\bar{C}$  + ketene diethylacetal (30% yield together with other prods.) see (229).]

Reaction of  $\bar{C}$  with acids or their salts. [ $\bar{C}$  on htg. with NaOAc or other metal salts of AcOH yields acetic anhydride (1:1015); this reactn. is well known and will not be amplified here;  $\bar{C}$  with salts of acids other than acetic gives in some cases the corresp. mixed anhydride, in others only the anhydride of the second acid. E.g.,  $\bar{C}$  (1 mole) with dry Na isovalerate (1 mole) gives at 130° the mixed anhydride contg. 1 acetyl and 1 isovaleroyl radical (231); on the other hand,  $\bar{C}$  with dry Na cinnamate gives only cinnamic anhydride (231); many other examples are known.]

[ $\bar{C}$  on htg. with AcOH under appropriate conditions (232) (233) (234) loses HCl giving good yields  $Ac_2O$  (1:1015).]

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(263)  $\text{EtHgCl} + \text{butanone-2}$  (1:5405), but  $\bar{\text{C}}$  with dibenzylmercury or with benzylmercuric chloride shows little reaction (262) even after refluxing 2 weeks.]

[ $\bar{\text{C}}$  with tetraphenyltin in s.t. at  $100^\circ$  for 15 hrs. gives (very small yield (264)) of acetophenone (1:5515); for reactn. of  $\bar{\text{C}}$  with tetraethyllead and use in defn. of latter in gasoline see (265).]

[ $\bar{\text{C}}$  with triphenylbismuth in  $\text{CCl}_4$  yields (266) acetophenone (1:5515).]

[ $\bar{\text{C}}$  (2 moles) with  $\text{Ni}(\text{CO})_4$  (1 mole) in pet. ether gives (267)  $4\text{CO} + \text{NiCl}_2 + \text{biacetyl}$  the latter sep. as a 1:1 addn. cpd. with the  $\text{NiCl}_2$ .]

⑤ Acetanilide: cryst. from hot aq., m.p.  $114^\circ$ . [From  $\bar{\text{C}}$  with aniline (2 moles) followed by recrystallization to remove aniline hydrochloride. Note that even with aniline + aq. at room temp. acetanilide formn. occurs to extent of 35–45% but its proportion diminishes with increase of temp. (268).]

⑥ Acet-*p*-toluidide: cryst. from hot aq. or dil. alc., m.p.  $153^\circ$ . [From  $\bar{\text{C}}$  + *p*-toluidine (2 moles) followed by recrystallization to remove *p*-toluidine hydrochloride.]

⑦ Acet- $\alpha$ -naphthalide: m.p.  $159^\circ$ .

⑧ Acet- $\beta$ -naphthalide: m.p.  $132^\circ$ .

—  $\beta$ -Acetophenylhydrazide ( $\beta$ -acetylphenylhydrazine) ( $\text{C}_6\text{H}_5\text{NH.NH.COCH}_3$ ) [Beil. XV-241, XV<sub>1</sub>-(63)]: m.p.  $128$ – $129^\circ$ . [Note that  $\alpha$ -acetophenylhydrazide [Beil. XV-236, XV<sub>1</sub>-(62)], m.p.  $124^\circ$ , is obtd. from  $\alpha,\beta$ -diacetylphenylhydrazine [Beil. XV-245, XV<sub>1</sub>-(64)], m.p.  $107$ – $108^\circ$ , by partial hydrolysis.]

—  $\beta$ -Acet-*p*-nitrophenylhydrazide [Beil. XV-478]: yel. ndls. from alc., m.p.  $205$ – $206^\circ$ .

—  $\beta$ -Acet-2,4-dinitrophenylhydrazide [Beil. XV-492]: yel. pr. from alc., m.p.  $201^\circ$  (269).

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## 3:7070 1-CHLOROBUTEN-3-YNE-1

C<sub>4</sub>H<sub>3</sub>Cl

Beil. S.N. 13

(1-Chloro-2-vinylacetylene) CH<sub>2</sub>=CH-C≡C-Cl

B.P.

55-57° at 760 mm. (1) (2) (3) (4)

 $D_4^{20} = 1.0032$  (1) (2)  $n_D^{20} = 1.4663$  (1) (2)  
1.0034 (4) $D_4^{25} = 1.021$  (4)  $n_D^{25} = 1.4608$  (4)

Colorless oil, not explosive when pure (3) (4). —  $\bar{C}$  rapidly polymerizes on stdg. into black brittle solid sensitive to heat and shock (1); polymerization of  $\bar{C}$  catalyzed by u.v. light, peroxide, ozonides, etc. (2). After addn. of hydroquinone (3)  $\bar{C}$  can be distd. at ord. press.

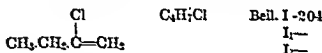
[For prepn. of  $\bar{C}$  from vinylacetylene by actn. of alkaline alk. hypochlorite solns. at 0° (yield 60-65% (4), 10% (1)) see (1) (2) (3) (4).]

$\bar{C}$  treated as directed at  $-10^\circ$  with conc.  $HCl + CuCl + NH_4Cl$  gives (56% yield (4)) 1,2-dichlorobutadiene-1,3 (3:9057) q.v.

$\bar{C}$  with  $NH_4OH/AgNO_3$  gives a white ppt.; with Ilseway reagent a yel. ppt. (4).

3:7070 (1) Jacobson, Carothers, *J. Am. Chem. Soc.* **55**, 4667-4669 (1933). (2) Jacobson (to du Pont), U.S. 1,967,861, July 24, 1934; *Cent.* 1936, 1 1709; *C.A.* **28**, 5534 (1934). (3) Klebanskii, Tsyurikh, Dolgopolskii, *Bull. acad. sci. U.R.S.S.* 1935, No. 2, 189-226; *Rubber Chem. Tech.* **9**, 1936. (4) Klebanskii, Volkenshtein, Orlova, 1936, 1 3414; *C.A.* **30**, 1023 (1936); *J. prakt.*

### 3:7075 2-CHLOROBUTENE-1



B.P.

58.4-58.6° at 760 mm. (1)

$D_4^{21} = 0.8950$  (2)

$n_D^{21} = 1.4115$  (2)

57-59° at 748 mm. (2)

$D_4^{15} = 0.9107$  (1)

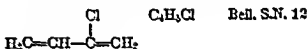
$n_D^{14.1} = 1.4166$  (1)

$\bar{C}$  forms with abs. EtOH an azeotrope, b.p. 53.6-54.0° at 760 mm.,  $D_4^{15} = 0.8945$ , contg. 58.5% by wt. of  $\bar{C}$  (1).

[For formn. from *d,l*-1,2-dichlorobutane (3:7680) + alc. KOH (together with *cis*- (3:7110) and *trans* (3:7110) stereoisomers of 1-chlorobutene-1) see (1).]

3:7075 (1) Navez, *Bull. soc. chim. Belg.* **39**, 435-443 (1930). (2) Kroegeer, Sowa, Nieuwland, *J. Org. Chem.* **1**, 167 (1936).

### 3:7080 2-CHLOROBUTADIENE-1,3 (Chloroprene)



B.P.

59.4° at 760 mm. (1)

$D_4^{20} = 0.9585$  (2)

$n_D^{20} = 1.4583$  (1)

46.9° at 600 mm. (1)

1.4570 (31)

49.5° at 400 mm. (1)

$D_4^{20} = 0.9583$  (1)

1.4163 (2)

32.8° at 300 mm. (1)

0.9573 (31)

6.4° at 100 mm. (1)

Colorless liq. with ethereal odor suggesting  $C_2H_5Br$ . Only slightly sol. aq. but miscible with most org. solvs.

$\bar{C}$  was first reported in 1931 (1) and given the name chloroprene (1) because of its analogy to 2-methylbutadiene-1,3 (isoprene) in structure and reactions. Despite its immense practical importance in the manufacture of various types of synthetic rubbers and plastics, comparatively little information on  $\bar{C}$  itself has been released for publication in the scientific literature.

[For a study of the toxicity and pathology of  $\bar{C}$  see (3); for study of poisoning by  $\bar{C}$  and its treatment see (4).]

[For studies of detn. of  $\bar{C}$  (5) by diazometric methods (6) (7) see indic. refs.]

### PREPARATION OF $\bar{C}$

$\bar{C}$  has been prepared from vinylacetylene by addn. of  $HCl$ , from dichlorobutenes by elimination of 1  $HCl$ , and from various other sources. Comparatively little on these methods has appeared in the scientific literature, and most of the information is available only through patents. Such of the latter as are here cited must be regarded only as illustrative as no guarantee of complete patent coverage can be offered.

From vinylacetylene.  $\bar{C}$  is formed from vinylacetylene (8) by addn. of HCl from aqueous soln. in pres. of catalysts (usually copper salts). The initial step comprises 1,4 addition, and the primary product is 4-chlorobutadiene-1,2 (isochloroprene) (3:7225). Under certain conditions this may be isolated as the major reaction product, but it readily isomerizes (especially in the presence of cuprous chloride and/or other salts (9)) yielding chloroprene. When sufficient amounts of HCl are present further addition to  $\bar{C}$  may also occur leading to 2,4-dichlorobutene-2 (3:5550) (see also below).

[For prepn. of  $\bar{C}$  from vinylacetylene (8) with conc. aq. HCl in pres. of  $\text{Cu}_2\text{Cl}_2 + \text{NH}_4\text{Cl}$  at  $30^\circ$  for 4 hrs. (65% yield) see (1) (47); for studies of this process in foreign laboratories see (10) (11) (12) (2) (24). For examples of patents on this process see (13)–(23) incl. For analogous prepn. of certain homologs of  $\bar{C}$  such as 2-chloro-3-methylbutadiene-1,3 (3:7290) and 2-chloro-3,4-dimethylbutadiene-1,3, etc., see (25) cf. (26).]

From dichlorobutenes. [For prepn. of  $\bar{C}$  from 3,4-dichlorobutene-1 (1,2-dichlorobutene-3) (3:5350) with powdered KOH or alc. NaOH see (27) (28), for 2,3-dichlorobutene-1 (3:9074) by thermal dehydrochlorination at  $530^\circ$  without cat. see (29); from 2,4-dichlorobutene-2 (3:5550) by dehydrochlorination (and isomerization) in pres. of fused KOH at  $180$ – $190^\circ$  (30) or over silica gel or clay at  $245$ – $275^\circ$  (31) cf. (30) see indie refs.; from 1,2-dichlorobutenes by dehydrochlorination with inorg. or org. bases in pres. of org. solvs. see (32).]

From other sources. [For prepn. of  $\bar{C}$  from 2,2,3-trichlorobutane (3:5680) by thermal dehydrochlorination over  $\text{MgCl}_2/\text{MgSO}_4$  cat. see (33); from polychlorobutenes of 55–66% chlorine content (corresp. to dichloro- and trichlorobutenes) by thermal dehydrochlorination at  $400$ – $500^\circ$  see (34) (note that 1-chlorobutadiene-1,3 (3:7210) is also formed; for separation of it from  $\bar{C}$  see (35)); for formn. of  $\bar{C}$  from vinyl chloride (3:7010) with acetylene in pres. of aq.  $\text{Cu}_2\text{Cl}_2/\text{NH}_4\text{Cl}$  see (36).]

## CHEMICAL BEHAVIOR OF $\bar{C}$

### ADDITION REACTIONS

With chlorine. [ $\bar{C}$  (2 moles) with  $\text{Cl}_2$  (1 mole) in  $\text{CHCl}_3$  at  $-10^\circ$  in pres. of hydroquinone gives mainly (37) cf. (38) (39) 1,2,4-trichlorobutene-2 (1,3,4-trichlorobutene-2) (3:9062) accompanied by other products such as 1,2,3-trichlorobutene-1 (37), b.p.  $40$ – $42^\circ$  at 10 mm.,  $D_4^{15} = 1.3190$ ,  $n_D^{15} = 1.4902$  (giving on oxidn.  $\alpha,\beta$ -dichloropropionic acid); note: data also consistent with 2,3,4-trichlorobutene-1 (3:9064) and 1,2-dichlorobutadiene-1,3 (3:9057), b.p.  $45$ – $48^\circ$  at 10 mm. (37),  $D_4^{15} = 1.1905$ ,  $n_D^{15} = 1.5065$  (37).]

With bromine. [ $\bar{C}$  (0.3 mole) with  $\text{Br}_2$  (0.25 mole) in  $\text{CHCl}_3$  at  $0$ – $5^\circ$  gives mainly (40) 2-chloro-1,4-dibromobutene-2, b.p.  $98$ – $101^\circ$  at 10 mm. (oxidizing with  $\text{KMnO}_4$  to bromoacetic acid), accompanied by other products; note that in pres. of anti-oxidants distn. range of prod. is much wider perhaps owing to formn. of geom. stereoisomers.]

With iodine chloride. [ $\bar{C}$  with  $\text{ICl}$  in  $\text{CHCl}_3$  at  $-5^\circ$  to  $0^\circ$  gives (70% yield (41)) a prod. regarded as 2,4-dichloro-1-iodobutene-2.]

With hydrogen chloride. [ $\bar{C}$  with conc. aq. HCl in pres. of  $\text{Cu}_2\text{Cl}_2$  (42) adds HCl giving 2,4-dichlorobutene-2 (3:5550); for behavior of  $\bar{C}$  in liq. HCl see (43).]

With hydrogen bromide. [ $\bar{C}$  (0.96 mole) with dry HBr (0.88 mole) in AcOH at  $-5^\circ$  gives (72% yield on  $\text{Br}_2$  (44)) 2-chloro-4-bromobutene-2, b.p.  $150$ – $152^\circ$ ;  $D_4^{20} = 1.5264$ ,  $D_4^{15} = 1.5335$ ;  $n_D^{15} = 1.5160$ ,  $n_D^{15} = 1.5185$ ; note that this prod. with aq.  $\text{KMnO}_4$  oxidizes to AcOH + bromoacetic acid and adds 1 mole  $\text{Br}_2$  giving 2-chloro-2,3,4-tribromobutane, b.p.  $104.5$ – $106^\circ$  at 10 mm.,  $D_4^{15} = 2.1907$ .]

With hydrochlorous acid. [The behavior of  $\bar{C}$  with  $\text{HOCl}$  appears not to have been reported; 1,4 addition to  $\bar{C}$  might be expected to yield 1,2-dichlorobuten-2-ol-1 and/or 2,4-dichlorobuten-2-ol-1, but neither is reported from any source; an isomer, viz., 2,3-







II-151, II<sub>1</sub>-(70), II<sub>2</sub>-(163)], b.p. 117-118° (3); for corresp. react. with Pb propionate or Na *n*-butyrate see (3).]

[ $\bar{C}$  in  $C_6H_6$  with  $ZnCl_2$  +  $HCl$  gas at 55-65° gives (52) cf. (28) benzyl chloride (3:8535). —  $\bar{C}$  with chlorobenzene (3:7003) + dehydrating agts. gives (28) *p*-chlorobenzyl chloride (3:0220). —  $\bar{C}$  with toluene +  $SnCl_4$  gives (35-40% yield (53)) *p*-methylbenzyl chloride (*p*-xylyl chloride) (3:8660) together with other prods.]

[ $\bar{C}$  in  $AcOH$  soln. without cat. condenses with aromatic nuclei: e.g.,  $\bar{C}$  with toluene in  $AcOH$  gives (25% yield (15)) a mixt. of *o*-xylyl chloride (3:8710) and *p*-xylyl chloride (3:8660); for analogous reactns. of  $\bar{C}$  in  $AcOH$  with *o*-xylene (1:7430), *m*-xylene (1:7420), pseudocumene (1:7470), mesitylene (1:7455), naphthalene (1:7200), tetralin (1:7550), anisole (1:7445), etc., see (15).]

[By virtue of its reactive halogen atom  $\bar{C}$  reacts readily with Grignard reagents giving (54) the corresp. methyl ethers: e.g.,  $\bar{C}$  with *n*-BuMgBr gives (67% yield (55)) (56) *n*-amyl methyl ether (1:7905);  $\bar{C}$  (2 moles) with decamethylene-bis-MgBr gives (53% yield (57)) dodecanediol-1,12-dimethyl ether;  $\bar{C}$  with  $CH_3-C\equiv C-MgBr$  gives (58)  $CH_3.C\equiv C.CH_2OCH_3$ ;  $\bar{C}$  with  $Br-Mg.C\equiv C-MgBr$  gives (63% yield (32)) 1,4-dimethoxybutyne-2;  $\bar{C}$  with  $C_6H_5MgBr$  gives (60% yield based on initial  $C_6H_5Br$  (59)) benzyl methyl ether (1:7475);  $\bar{C}$  with benzyl  $MgCl$  gives mainly (60) cf. (61) (62) methyl  $\beta$ -phenylethyl ether ( $\omega$ -methoxyethylbenzene) (Beil. VI-479, VI<sub>1</sub>-(238)], b.p. 185-187° (61), accompanied by some *o*-tolylcarbinol methyl ether and *p*-tolylcarbinol methyl ether, cf. (60).]

[In the pres. of appropriate catalysts  $\bar{C}$  adds to olefinic unsatd. linkages, addition occurring as if  $\bar{C}$  dissociated into  $(Cl\cdot)$  and  $(CH_3O\cdot CH_2\cdot)$  radicals; examples of these addition reactions are given as follows:  $\bar{C}$  with ethylene +  $BiCl_3$  at 80° under 700-800 lbs. press. for 7 hrs. gives (63)  $\gamma$ -chloro-*n*-propyl methyl ether;  $\bar{C}$  with propylene +  $BiCl_3$  similarly gives (63)  $\gamma$ -chloro-*n*-butyl methyl ether;  $\bar{C}$  with 2-methylpropene-1 (isobutylene) +  $HgCl_2$  on stdg. in s.t. 4 days at room temp. gives (60% yield (64)) 2-chloro-4-methoxy-2-methylbutane, b.p. 136° at 751 mm.  $D_4^{20} = 0.9455$ , accompanied by some *tert*-butyl chloride (3:7045); but  $\bar{C}$  with isobutylene +  $TiCl_4$  as directed (65) gives the corresp. alc., viz., 3-chloro-3-methylbutanol-1;  $\bar{C}$  with 2-methylbutene-2 (trimethylethylene) (1:8220) with  $ZnCl_2$  as directed (63) or with  $HgCl_2$  in s.t. at room temp. for 48 hrs. (64) gives (40% yield (64)) 2-chloro-4-methoxy-2,3-dimethylbutane, b.p. 153° at 761 mm., 46-46.5° at 14 mm.,  $D_4^{20} = 0.9528$ , accompanied by some *tert*-AmCl (3:7220);  $\bar{C}$  with cyclohexene (1:8070) +  $ZnCl_2$  in  $CS_2$  stirred 5 hrs. at 0°, then 3 hrs. at room temp., gives (28.7% yield (66)) cf. (64) (*o*-chlorocyclohexyl)methyl methyl ether (2-chloro-1-(methoxymethyl)cyclohexane), b.p. 88-91° at 17 mm.,  $D_4^{20} = 1.1552$  (66).]

[ $\bar{C}$  with butadiene-1,3 +  $ZnCl_2$  in s.t. at room temp. for 21 hrs. gives (70% yield (64)) *n* mixt. of 1-chloro-5-methoxypentene-2, b.p. 168° at 758 mm., 56° at 10 mm.,  $D_4^{20} = 1.0022$  (from 1,4- addn. (?)) + 3-chloro-5-methoxypentene-1, b.p. 148° at 756 mm., 35° at 10 mm.,  $D_4^{20} = 0.9740$  (from 1,2 addn. (?)) (note that these two prods. represent synionic mesomers);  $\bar{C}$  with cyclohexadiene-1,3 (1:8057) +  $HgCl_2$  under  $CO_2$  at 0° stood 24 hrs. gives (38% yield (64)) (4-chlorocyclohexenyl)methyl methyl ether, b.p. 81° at 10 mm.,  $D_4^{20} = 1.0636$  (64).]

[ $\bar{C}$  (1 mole) + vinylacetylene (1 mole) +  $BiCl_3$  (trace) + pyrogallol (trace) in dry ether nt 5-15° for 9 hrs. (with periodic addns. of  $BiCl_3$ ) gives (67) 34.8% yield 1-chloro-5-methoxy-1,3-pentadiene-2, b.p. 61° at 10 mm.,  $D_4^{20} = 1.0127$ ,  $n_D^{20} = 1.4893$  (by 1,4 addn.), (67) 1-chloro-5-methoxypentadiene-1,3, b.p. 46° at 10 mm.,  $D_4^{20} = 1.0022$  (from 1,4 addn. (?)) with other prods.; note that of the two preceding dienes the former with  $Cu_2Cl_2$  +  $HCl$  in ether at 20-40° for 2 hrs. readily isomerizes (81% yield (67)) to the latter; for further reactions of the pair see (67).]

[ $\bar{C}$  with 4.67% dislvd.  $ZnCl_2$  shaken with  $CO$  at 25-50° nt 275-625 pounds press. for 8 hrs. gives (63) methoxyacetyl chloride (3:5225).]

$\bar{C}$  with tertiary amines yields the corresp. quaternary ammonium salts: e.g.,  $\bar{C}$  with  $Me_3N$  in dry ether gives (69) methoxymethyl-trimethyl-ammonium chloride (chloroplatinate, m.p. 228–229°, picrate, m.p. 198°);  $\bar{C}$  with pyridine in dry ether gives (69) methoxymethyl-pyridinium chloride (chloroplatinate, m.p. 182–185° (70), 180–182° dec. (35),  $HgCl_2$  cpd., m.p. 91° (69));  $\bar{C}$  with quinoline in  $CHCl_3$  gives (69) methoxymethyl-quinolinium chloride (chloroplatinate, m.p. 232–234°; chloroaurate, m.p. 126–127°); for other quaternary salts see (69).

- Methoxymethyl benzoate: oil, h.p. 283° (71). [From  $\bar{C}$  with  $NaOBz$  at 100° (71).]
- Methoxymethyl *p*-nitrobenzoate: unreported.
- Methoxymethyl 3,5-dinitrobenzoate: unreported.
- *S*-(Methoxymethyl)isothiourea picrate: m.p. 163° (72). [From  $\bar{C}$  + thiourea in cold acetone giving (90% yield (72)) corresp. hydrochloride, m.p. 112° dec., which is then converted to the picrate]
- *N*-(Methoxymethyl)phthalimide: cryst. from dry  $MeOH$ , m.p. 120–121° (73), 118° (74). [Prepn reported only by indirect means (73) (74)]

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(43) Smi

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(1941);

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(4) 3,

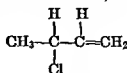
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### 3: 7090 *d,l*-3-CHLOROBUTENE-1

( $\gamma$ -Chloro- $\alpha$ -butylene;  
 $\alpha$ -methylallyl chloride)



$\text{C}_4\text{H}_7\text{Cl}$

Beil. I —

I<sub>1</sub>—

I<sub>2</sub>-(174)

B.P.

63° at 760 mm. (1)

$D_4^{20} = 0.0001$  (1)  $n_D^{20} = 1.4151$  (10)

64-65° (2)

1.4150 (5) (3) (2)

64° at 750 mm. (5)

1.4153 (1)

63.5° at 750 mm. (3)

1.4242 (4)

63.4-63.5° at 751 mm. (10)

24.2-24.6° at 178 mm. (3)

-5° at 26 mm. (4)

For important discussion of the relationship and conversion of  $\tilde{\text{C}}$  to 1-chlorobutene-2 see the latter (3:7205).

[For the prepn. of a mixt. of  $\tilde{\text{C}}$  and 1-chlorobutene-2 from butadiene-1,3 + HCl see (5) (1) (6) (7); for prepn. of  $\tilde{\text{C}}$  from methyl-vinyl-carbinol (buten-1-ol-3) + conc. HCl see (3) (4) (8).]

[For study of reaction with Mg, Zn, etc., see (9); for study of hydrolysis under various conditions see (10); for behavior with cuprous cyanide see (11).]

— Methyl-vinyl-carbinyl *p*-nitrobenzoate: m.p. 43-44° (12). [Note that this prod. has been prepd. only by indirect means (12) and may (because of allylic rearr.) possibly be in fact crotonyl *p*-nitrobenzoate (see under 3:7205).]

— Methyl-vinyl-carbinyl 3,5-dinitrobenzoate: unreported. [See also note under 3:7205.]

— *N*-(Methyl-vinyl-carbinyl)phthalimide: m.p. 87-88° (13). [Prepd. indirectly, and structure unproved (13).]

3:7090 (1) Henne, Chanan, Turk, *J. Am. Bull. soc. chim. Belg.* 31, 168 (1922). (3) 1 (1942). (4) Böhme, *Ber.* 71, 2378-2379 (1942). (5) Voigt, *J. p. Chem.* 2, 494-496 (1938). (6) Pont), U.S. 2,123,504, July 12, 1938; *Cent J. Indian Chem. Soc.* 13, 584 (1936). (9) Y (10) Young, Andrews, *J. Am. Chem. Soc.* 66, 421-425 (1944).

(11) Lane, Fentress, Sherwood, *J. Am. Chem. Soc.* 66, 545-548 (1944). (12) Burton, *J. Chem. Soc.* 1929, 456. (13) Mumm, Richter, *Ber.* 73, 847, 857 (1940).

### 3: 7100 3-CHLOROPROPYNE-1

(Propargyl chloride)



$\text{C}_3\text{H}_3\text{Cl}$

Beil. I - 248

I<sub>1</sub>—

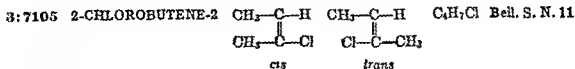
I<sub>2</sub>—

B.P. 65° (1)

$D_4^{25} = 1.0454$  (1)

[For prepn. from propyn-2-ol-1 (propargyl alcohol) [Beil. I-454, I<sub>r</sub>-(234) with  $\text{PCl}_3$  see (1) (2).]

3:7100 (1) Henry, *Ber.* 8, 398 (1875). (2) Pauling, Gardy, Saylor, *J. Am. Chem. Soc.* 64, 1753-1756 (1942).



*cis* Stereoisomer

B.P.	F.P.				
66.6-67.0° at 760 mm.	(1) -117.3° (18)	$D_4^{20} = 0.0239$ (18)	$n_D^{20} = 1.4240$ (18)		
70.58°	(18)	$D_4^{16} = 0.9246$ (1)			
		$D_4^0 = 0.0420$ (1)	$n_D^{13.4} = 1.4250$ (1)		

*trans* Stereoisomer

B.P.	F.P.				
62.4-62.8° at 760 mm.	(1) -105.8° (18)	$D_4^{20} = 0.9139$ (18)	$n_D^{20} = 1.4190$ (18)		
62.84°	(18)	$D_4^{16} = 0.9185$ (1)			
		$D_4^0 = 0.9301$ (1)	$n_D^{13.4} = 1.4217$ (1)		

Ordinary  $\bar{\text{C}}$  (mixt.)

B.P.					
64-68°	(2)	$D_4^{20} = 0.9179$ (3)			
62-67°	(3)		$n_D^{15} = 1.4232$ (2)		
59-61° at 761 mm.	(4)	$D_4^{15} = 0.9220$ (2)			

Both stereoisomers form with abs. EtOH const.-boilg. mixts from which  $\bar{\text{C}}$  can be recovered by repeated shaking with 3 vols. aq. to remove the alc., the azeotrope with *cis*- $\bar{\text{C}}$ , b.p. 60.0-60.4° at 760 mm.,  $D_4^{15} = 0.8964$ , conts. 81.6% by wt. of *cis*- $\bar{\text{C}}$ , the azeotrope with *trans*- $\bar{\text{C}}$ , b.p. 56.8-57.2° at 760 mm.,  $D_4^{15} = 0.8960$ , conts. 84.6% by wt. of *trans*- $\bar{\text{C}}$  (1).

[For study of toxicity of  $\bar{\text{C}}$  see (5); for use as anthelmintic see (6).]

[For prepn. of the two geom. stereoisomers of  $\bar{\text{C}}$  from either *d,l*- (3:7615) or *meso*- (3:7680) 2,3-dichlorobutane with alc. KOH (1 mole + 25% excess) refluxed for 3 days see (1).]

[For prepn. of ord.  $\bar{\text{C}}$  (mixt. of *cis* + *trans* stereoisomers) from 2,2-dichlorobutane (3:7415) with alc. KOH see (8), from ord. 2,3-dichlorobutane (3:7615) with alc. KOH (1) (2) (3) (8) (9), with aq.  $\text{NaHCO}_3$  +  $\text{Na}_2\text{CO}_3$  under press. (yield 20%  $\bar{\text{C}}$  accompanied by 4% butanone-2 (ethyl methyl ketone) (1:5405) + 5% butenols (7), with aq. alkali or alkaline-earth hydroxides under press. at 118-250° (10), by passing vapor over  $\text{BaCl}_2$  at 200-300° (11), or by passing vapor + steam at 300-400° over silica gel contg.  $\text{MgCl}_2$  +  $\text{CaCl}_2$ , etc. (yields 21-25%  $\bar{\text{C}}$  accompanied by 35-38% butadiene-1,3 and 6-8% butanone-2) (3) see indic. refs.; from butanone-2 (ethyl methyl ketone) (1:5405) with  $\text{PCl}_3$  ( $\bar{\text{C}}$  is accompanied by 2-chlorobutene-1 (3:7075) (12) and by 2,2-dichlorobutane (3:7415) (4)) see indic. refs.]

[For prepn. of  $\bar{\text{C}}$  from 2,2-dichloro-3-iodobutane (see below) with alc. KOH see (2); from 2-bromo-2-chloro-3-iodobutane with alc. KOH see (2) (note that the isomeric 2-bromo-3-chloro-2-iodobutane under same circumstances gives 3-bromo-2-chlorobutene-2).]

[For prepn. of  $\bar{\text{C}}$  from 2,3-dichlorobutene-2 (3:5500) with aq. alk. or alkaline-earth hydroxides under press. at 118-250° see (13).]

If  $\bar{\text{C}}$  with Cl may add halogen, or be further substituted by halogen, or both, according to:

circumstances: e.g.,  $\bar{C}$  in liq. phase with  $Cl_2$  at 20–40° in absence of light but in pres. of cat. such as  $SnCl_4$  or  $FeCl_3$  adds  $Cl_2$  giving (14) 2,2,3-trichlorobutane (3:5680);  $\bar{C}$  in liq. phase with  $Cl_2$  in pres. of light and of  $O_2$  (15) or  $\bar{C}$  with  $Cl_2$  in pres. of  $NaHCO_3$  at 0° (4) substitutes further giving (55% yield (4)) (15) 2,3-dichlorobutene-1 (3:0074) (accompanied by 45% 2,2,3-trichlorobutane (3:5680) (4));  $\bar{C}$  with  $Cl_2$  at 350° gives (16) a mixt. of unsatd. chlorobutenes, probably 1,2-dichlorobutene-2 (3:5360) or (3:5615) and 1,3(2,4)-dichlorobutene-2 (3:5550).]

$\bar{C}$  adds  $Br_2$  yielding (2) 2,3-dibromo-2-chlorobutane, b.p. 182.5–180° sl. dec., 60–60.5° at 12 mm.,  $D_4^{15} = 1.8975$ ,  $n_D^{15} = 1.5339$  (2) (this prod. with alc. KOH loses  $HBr$  yielding (2) 3-bromo-2-chlorobutene-2, b.p. 128–129.5°,  $D_4^{15} = 1.4998$ ,  $n_D^{15} = 1.4950$  (2)).

$\bar{C}$  adds  $ICl$  yielding (2) 2,2-dichloro-3-iodobutane, b.p. 69.5° at 11.5 mm.,  $D_4^{15} = 1.8580$ ,  $n_D^{15} = 1.5595$  (2) (this prod. with KOH regenerates  $\bar{C}$ ).]

$\bar{C}$  also adds  $HOCi$  but from the addn. prod.  $HCl$  splits out immediately: e.g.,  $\bar{C}$  in  $CCl_4$  with  $Cl_2$  + aq. as directed (17) gives (85% yield (17)) 3-chlorobutanone-2 ( $\alpha$ -chloroethyl methyl ketone) (3:7598).]

[For behavior of  $\bar{C}$  with dry  $HF$  yielding 2,2-difluorobutane see (18).]

$\bar{C}$  with steam passed at 300–400° over silica gel contg.  $MgCl_2$  +  $CuCl_2$  is unchanged (3) (dif. from 3-chlorobutene-1 (3:7090) or 1-chlorobutene-2 (3:7205) which lose  $HCl$  yielding butadiene-1,3 (3)). — Note that with alc. KOH the *cis*- $\bar{C}$  splits off  $HCl$  2.5 times as fast as the *trans*- $\bar{C}$  (1).] [For dehydrohalogenation of  $\bar{C}$  yielding butadiene-1,3 see (19) (20).]

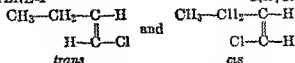
$\bar{C}$  with alcoholates or phenolates as directed (9) yields the corresp. ethers; e.g.,  $\bar{C}$  with  $NaOEt$  yields (9)  $\alpha,\beta$ -dimethylvinyl ethyl ether.]

$\bar{C}$  on oxidn. with boilg. aq.  $KMnO_4$  yields (12) acetic acid (1:1019) and propionic acid (1:1025); the *cis*- $\bar{C}$  appears to give mainly acetic acid; the *trans*- $\bar{C}$  gives mainly propionic acid (12).

3:7105 (1) Naves, *Bull. soc. chim. Belg.* 39, 435–443 (1930); *Cent.* 1931, I 1269–1270; *C.A.* 25, 2412 (1931). (2) Petrov, Sapozhnikova, *J. Gen. Chem. (U.S.S.R.)* 7, 470–484 (1937); *Cent.* 1937, I 4025; *C.A.* 31, 4203 (1937). (3) Gutner, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 6, 1720–1735 (1936); *Cent.* 1937, I 3780; *C.A.* 31, 4265 (1937). (4) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232–1216 (1938); *Cent.* 1939, II 4222–4223, *C.A.* 33, 4190 (1939). (5) McCawley, *Univ. Calif. Pub. Pharmacol.* 2, 89–97 (1912); *C.A.* 36, 4911 (1912). (6) Marcenac, *Compt. rend.* 198, 510–512 (1934); *Cent.* 1934, I 2780; *C.A.* 28, 2800 (1934). (7) Dobryanskii, Gutner, Shchigel'skaya, *J. Gen. Chem. (U.S.S.R.)* 7, 1315–1320 (1937); *Cent.* 1938, I 501, *C.A.* 31, 6180 (1937). (8) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 7, 603–600 (1937); *Cent.* 1937, II 372; *C.A.* 31, 5754 (1937). (9) I.G., *Brit.* 332,605, Aug. 21, 1930; *Cent.* 1930, II 2572. (10) du Pont Co. & Cass, *Brit.* 549,709, Dec. 8, 1912; *C.A.* 38, 766 (1914).

(11) Levine, Cass (to du Pont Co.), U.S. 2,323,226, June 20, 1943; *C.A.* 38, 119 (1944); *Brit.* 535,585, April 15, 1941; *C.A.* 39, 1337 (1942). (12) Charpentier, *Bull. soc. chim.* (5) 1, 1407–1411 (1931). (13) Cass (to du Pont Co.), U.S. 2,291,375, July 28, 1942; *C.A.* 37, 650 (1942). (14) Levine, Cass (to du Pont Co.), U.S. 2,323,237, June 29, 1943; *C.A.* 38, 119 (1944); *Brit.* 535,580, April 15, 1941; *C.A.* 36, 1937 (1942). (15) Hearne (to Shell Development Co.), U.S. 2,269,614, Sept. 22, 1912; *C.A.* 37, 1120 (1913). (16) N. V. de Batavische Petroleum Maatschappij, *Brit.* 408,010, July 22, 1937; *Cent.* 1937, II 4102; *C.A.* 31, 8543 (1937); *French* 810,112, March 15, 1937; *Cent.* 1937, II 4102; *C.A.* 32, 587 (1938). (17) Groll, Hearne (to Shell Development Co.), U.S. 2,000,303, Nov. 10, 1936; *Cent.* 1937, I 4154; *C.A.* 31, 419 (1937); *Brit.* 437,573, Nov. 28, 1935; *French* 787,629, Sept. 21, 1935; *Cent.* 1936, II 2227. (18) Henne, Hinkamp, *J. Am. Chem. Soc.* 67, 1191–1197 (1945). (19) Evans, Morris, Melchior (to Shell Development Co.), U.S. 2,370,007, July 3, 1945; *C.A.* 39, 4331 (1945). (20) Hearne (to Shell Development Co.), U.S. 2,370,708, July 3, 1945; *C.A.* 39, 4330 (1945).

## 3:7110 1-CHLOROBUTENE-1

C<sub>4</sub>H<sub>7</sub>Cl Beil. S. N. 11*trans* Stereoisomer

B.P.

68.0-68.2° at 760 mm. (1)

$$D_4^{15} = 0.9205 \quad (1) \quad n_D^{14.6} = 1.4225 \quad (1)$$

$$D_4^{20} = 0.9376 \quad (1)$$

*cis* Stereoisomer

B.P.

63.4-63.0° at 760 mm. (1)

$$D_4^{15} = 0.9153 \quad (1) \quad n_D^{15} = 1.4194 \quad (1)$$

$$D_4^{20} = 0.9329 \quad (1)$$

Both stereoisomers form with abs. EtOH const.-boil. mixts from which  $\bar{C}$  can be recovered by repeated shaking with 3 vols. aq. to remove the alc.: the azeotrope with the *trans* form, b.p. 61.2-61.6° at 760 mm,  $D_4^{15} = 0.8912$ , conts. 79.8% by wt. of  $\bar{C}$ ; the azeotrope with the *cis* form, b.p. 57.0-58.2° at 760 mm,  $D_4^{15} = 0.8946$ , conts. 85.2% by wt. of  $\bar{C}$  (1).

[For formn. of both *trans* and *cis* forms of  $\bar{C}$  from *d,l*-1,2-dichlorobutane (3:7080) with alc. KOH (1 mole + 25% excess) refluxed 3 days (some 2-chlorobutene-1 (3:7075) is also formed) see (1)]

[The *cis* form of  $\bar{C}$  with alc. KOH splits off HCl 2.9 times as fast as the *trans* form (1).]

[ $\bar{C}$  with Cl<sub>2</sub> in dark at 10° gives (70-75% yield (2)) 1,1,2-trichlorobutane, but no constants for latter can be found either in (2) or in prior literature]

3:7110 (1) Navez, *Bull. soc. chim. Belg.* 39, 435-443 (1930), *Cent.* 1931, I 1269-1270; *C.A.* 25, 2412 (1931) (2) Henne, *Hunkamp J Am Chem Soc.* 67, 1197 (1945).

## 3:7120 1-CHLORO-2-METHYLPROPENE-1

C<sub>4</sub>H<sub>7</sub>Cl Beil. I - 209

(*β,β*-Dimethylvinyl chloride;  
isocrotyl chloride;  
 $\alpha$ -chloroisobutylene)



I—  
I<sub>2</sub>—

B.P.

68-69° at 775 mm. (1)

$$D_4^{25} = 0.9144 \quad (3) \quad n_D^{25} = 1.4198 \quad (3)$$

68.1° (2) (5)

66.9° at 757 mm. (3)

$$D_4^{20} = 0.9180 \quad (2) \quad n_D^{20} = 1.4221 \quad (2)$$

65-68° (4)

$$0.918 \quad (6) \quad 1.422 \quad (7)$$

[See also 3-chloro-2-methylpropene-1 (3:7145)]

Note that for  $\bar{C}$  the designation *β,β*-dimethylvinyl chloride is now preferred, cf. (5); great care should be used to avoid confusion of  $\bar{C}$  with the isomeric and very closely related 3-chloro-2-methylpropene-1 (methallyl chloride) (3:7145); both these compounds are now commercial chemicals in the U.S.A.

[For prepn. of  $\bar{C}$  from 3-chloro-2-methylpropene-1 (methallyl chloride) (3:7145) see (2) (3): e.g., methallyl chloride (10 moles) with 80% H<sub>2</sub>SO<sub>4</sub> (1 mole) stirred at 40° for 2½ hrs. gives an upper phase contg 87%  $\bar{C}$  + 7% residual methallyl chloride + 6% dichlorides and polymers; after washing free from acid, drying, and distilling it yields 85%  $\bar{C}$  (8) (20)]

[For formn. of  $\bar{C}$  (usually accompanied by the isomeric methallyl chloride and/or other



prods.) from 2-methylpropene-1 (isobutylene) with  $\text{Cl}_2$  (5) (9); from 1,1-dichloro-2-methylpropane (isobutylidene dichloride) (3:7425) by actn. of  $\text{NH}_4\text{OH}$  or alc.  $\text{KOH}$  (4), from 1,2-dichloro-2-methylpropane (isobutylene dichloride) (3:7430) with alc.  $\text{KOH}$  (10) see indic. refs.]

[For formn. of  $\bar{\text{C}}$  (together with the isomeric methallyl chloride) from 1-chloro-2-methylpropanol-2 (isobutylene chlorohydrin) (3:7752) by soln. in cold 45%  $\text{H}_2\text{SO}_4$  and subsequent warming (giving 90%  $\bar{\text{C}}$  + 10% methallyl chloride (2) (8)), or by use of  $\text{P}_2\text{O}_5$  (11) cf. (12); from 1,1,1-trichloro-2-methylpropanol-2 (1,1,1-trichloro-*ter*-butyl alc. = "Chlore-tone") (3:2662) with Zn dust + boilg. alc. (13), or from isobutyraldehyde (1:0120) by actn. of  $\text{PCl}_5$  (4) see indic. refs.]

$\bar{\text{C}}$  forms with aq. a const.-boilg. mixt., b.p. 61.9°, contg. 7.5% aq. (2)

[For study of anesthetic props. of  $\bar{\text{C}}$  see (14).]

Reactions involving further substitution of H atoms in  $\bar{\text{C}}$ . [ $\bar{\text{C}}$  with  $\text{Cl}_2$  (in pres. of 1.5 moles  $\text{NaHCO}_3$  at 0° (15)) cf. (2) reacts not only by addn. but also by substitution (the latter involving a shift of double bond) giving respectively 32% 1,1,2-trichloro-2-methylpropane (3:5710) + 68% 1,1-dichloro-2-methylpropene-2 (3:7480).]

Reactions involving the double bond of  $\bar{\text{C}}$ . [ $\bar{\text{C}}$  adds  $\text{Cl}_2$  (see preceding paragraph).]

[ $\bar{\text{C}}$  also adds  $\text{HOCl}$  (chlorohydration); e.g.,  $\bar{\text{C}}$  with  $\text{Cl}_2$  + aq., or aq.  $\text{HOCl}$ , or even alkyl or alkyl hypochlorites as directed (16) cf. (2) (4), yields 1,1-dichloro-2-methylpropanol-2 ( $\beta,\beta$ -dichloro-*ter*-butyl alc.) (3:5772), b.p. 150°.]

[ $\bar{\text{C}}$  can also undergo catalytic hydration of the double bond; e.g.,  $\bar{\text{C}}$  (1 mole) with 90%  $\text{H}_2\text{SO}_4$  (1 mole) stirred at -10° to 0° for 2½ hrs., then poured onto cracked ice, diluted with aq., and distilled, gives 66% of the initial  $\bar{\text{C}}$  as 1-chloro-2-methylpropanol-2 ( $\beta$ -chloro-*ter*-butyl alcohol) (isobutylene chlorohydrin) (3:7752); note that other acids can also be used for this hydration, e.g., 85%  $\text{H}_3\text{PO}_4$ , 70%  $\text{HNO}_3$ , 60%  $\text{HClO}_4$ , benzenesulfonic acid, e.g., each having its own optimum conditions. Note also that some 18% of the initial  $\bar{\text{C}}$  is not hydrated but is partially isomerized to a mixt. contg. 90%  $\bar{\text{C}}$  + 10% methallyl chloride (2) (17).]

Reactions involving the halogen atom of  $\bar{\text{C}}$ . Note that in  $\bar{\text{C}}$  the halogen is extremely inert as compared with that of the isomeric methallyl chloride (3:7145); this permits removal of the latter from  $\bar{\text{C}}$  by chemical means (see below).

[ $\bar{\text{C}}$  is virtually unattacked by aq. or alc.  $\text{KOH}$  even at 100° (11) (1) (2) (dif. from methallyl chloride (3:7145)). —  $\bar{\text{C}}$  does not react with boilg. aq.  $\text{K}_2\text{CO}_3$  or  $\text{KOAc}$  (1) (dif. from methallyl chloride (3:7145)).]

[ $\bar{\text{C}}$  is not normally convertible to isobutyraldehyde except under extreme conditions (5) (dif. from methallyl chloride (3:7145) which upon acid hydrolysis or even boilg. with aq. gives isobutyraldehyde).]

—  $\beta,\beta$ -Dimethylvinyl (isocrotyl) acetate: unreported.

—  $\beta,\beta$ -Dimethylvinyl (isocrotyl) benzoate: unreported.

—  $\beta,\beta$ -Dimethylvinyl (isocrotyl) *p*-nitrobenzoate: unreported.

—  $\beta,\beta$ -Dimethylvinyl (isocrotyl) 3,5-dinitrobenzoate: unreported.

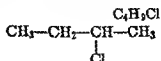
— *N*-( $\beta,\beta$ -dimethylvinyl)phthalimide: unreported.

3:7120 (1) Pogorabelski, *J. Russ. Phys.-Chem. Soc.* 36, 1129-1184 (1904); *Cent.* 1905, I 667-668. (2) Burgin, Hearne, Rust, *Ind. Eng. Chem.* 33, 385-388 (1941). (3) Hurdia, Smyth, *J. Am. Chem. Soc.* 65, 59 (1943). (4) *Oeconomidis, Compl. rend.* 92, 1237 (1881); *Bull. soc. chim.* (2) 35, 409-500 (1881). (5) Burgin, Engs, Groll, Hearne, *Ind. Eng. Chem.* 31, 1413-1419 (1939). (6) Engs, Redmond, U.S. 2,077,382, April 20, 1937; *Cent.* 1937, II 1660; *C.A.* 31, 3037 (1937). (7) Aschan, *Oversikt Finska Vetenskaps-Soc. Förh.* 58, 122 (1916). (8) Groll, Burgin (to Shell Development Co.), U.S. 2,042,223, May 26, 1936; *Cent.* 1937, I 1274; *C.A.* 30, 4875 (1936). (9) Tamele, Ott, Marple, Hearne, *Ind. Eng. Chem.* 33, 115 (1941). (10) Mouneyrat, *Ann. chim.* (7) 20, 633-634 (1900).

(11) Michael, *J. prakt. Chem.* (2) **64**, 104 (1901). (12) Krassuski, *J. prakt. Chem.* (2) **64**, 390 (1901); *J. Russ. Phys.-Chem. Soc.* **33**, 1-26 (1901); *Cent.* 1901, I 996. (13) Jozitsch, *J. Russ. Phys.-Chem. Soc.* **30**, 920-924 (1898); *Cent.* 1899, I 606. (14) Abreu, Peoples, Emerson, *Anaesthesia and Analgesia* **18**, 156-161 (1939); *Cent.* 1939, II 2111; *C.A.* **33**, 6959 (1939). (15) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **8**, 1232-1245 (1938); *Cent.* 1939, II 4222; *C.A.* **33**, 4190 (1939). (16) Groll, Hearne (to Shell Development Co.), U.S. 2,060,303, Nov. 10, 1936; *Cent.* 1937, I 4154; *C.A.* **31**, 419 (1937). N. V. de Bataafsche Petroleum Matschappij, Brit. 437,573, Oct. 31, 1935; *Cent.* 1936, II 2227; *C.A.* **30**, 2199 (1936). French 787,529, Sept. 24, 1935; *Cent.* 1936, II 2227; *C.A.* **30**, 1067 (1936). (17) Groll, Burga (to Shell Development Co.), U.S. 2,042,222, May 26, 1936; *Cent.* 1937, I 1546, *C.A.* **30**, 4875 (1936). N. V. de Bataafsche Petroleum Matschappij, French 791,644, Dec. 14, 1935, *Cent.* 1936, II 2227.

### 3:7125 *d,l*-2-CHLOROBUTANE

(*sec.*-Butyl chloride;  
ethyl-methyl-carbinyl chloride)



Beil. I - 119

$I_1$ —

$I_2$ -( 81)

B.P.		F.P.	
68.4-68.6° u.c.	(25)	-131.3° (1) (10)	$D_4^{25} = 0.86767$ (1)
68.25°	at 760 mm. (1) (2)		
68.1°	(3)		$D_4^{20} = 0.8740$ (5)
68.0-68.1°	(4)		0.87323 (1)
68°	at 761 mm. (5)		0.8726 (5)
68°	at 769 mm. (5)		0.8707 (6)
67.3-67.8° cor.	(6)		
67.3°	at 761.4 mm. (7)		$D_4^{15} = 0.87880$ (1)
67.2-67.3°	at 740 mm. (4)		$n_D^{25.2} = 1.3953$ (11)
67.2-67.7°	at 734 mm. (8)		
67.2°	at 764 mm. (7)		$n_D^{20} = 1.30709$ (5)
60.5°	at 731.8 mm. (9)		1.39694 (5)
			1.3969 (3)

(For b p. of C at various press. in range 49-285 mm. see (2).)

$n_D^{15} = 1.3994$  (1)

Liquid with agreeable ethereal odor.

[For prepn. of  $\bar{C}$  from butanol-2 (1:6155) by saturation with dry HCl gas and btg. in s.t. at 100° for several hrs. (9); by distillation with 18 wt. pts. 6 N HCl (50% yield (12)); with conc. HCl + ZnCl<sub>2</sub> (2 moles) (yields: 85-88% (13), 83% (14), 82% (5), 78% (15), 60-68% (16) (17)) (6); with PCl<sub>3</sub> + ZnCl<sub>2</sub> (yields: 67% (15), 40% (6)); with PCl<sub>5</sub> + ZnCl<sub>2</sub> (71% yield (15)); with SOCl<sub>2</sub> + pyridine (yields: 90% (15), 47% (5)); or with HCl in pres. of H<sub>3</sub>PO<sub>4</sub> (18) see indic. refs.]

[For formn. of  $\bar{C}$  from either butene-1 or butene-2 with HCl gas by addn. to unsatd. linkage (7) (19) in pres. of cat. (20) (21) (22) see indic. refs.; from *n*-butane with Cl<sub>2</sub> see (4) (23); from *n*-butylamine with HNO<sub>2</sub> (2.8% yield  $\bar{C}$  accompanied by 36.5% butenes, 25% butanol-1, 13.2% butanol-2, 5.2% *n*-butyl chloride (3:7160) and other prods.) see (24); from *sec.*-butylamine with NOCl in xylene see (25).]

[For study of anthelmintic props. of  $\bar{C}$  see (26).]

Pyrolysis of  $\bar{C}$ . [ $\bar{C}$  at 450-550° without cat. loses HCl and yields (4) (27) a mixt. contg. butene-1, *cis*-butene-2, and *trans*-butene-2 (dif. from 1-chlorobutane (3:7160) which gives only butene-1);  $\bar{C}$  at 450° in pres. of anhyd. CaCl<sub>2</sub> as cat. gives (4) (27) the same mixt. (as does also 1-chlorobutane (3:7160)). For use of this pyrolysis in distinction of  $\bar{C}$  from *ter*-butyl chloride (3:7045) see (23).]

Further halogenation of  $\bar{C}$ . [ $\bar{C}$  with  $Cl_2$  at 200–380° gives (28) a mixt. of dichlorobutanes contg. 1,3-dichlorobutane (3:7925), 2,2-dichlorobutane (3:7415), and d,l-2,3-dichlorobutane (3:7615) but no 1,2-dichlorobutane (3:7680); note, however, that  $\bar{C}$  with  $Cl_2$  in pres. of light gives (29) 1,2-dichlorobutane (3:7680), 1,3-dichlorobutane (3:7925), 2,2-dichlorobutane (3:7415), and both d,l- (3:7615) and meso- (3:7580) 2,3-dichlorobutanes.]

Reactions of the halogen atom of  $\bar{C}$ . [For study of rate of reactn. of  $\bar{C}$  with KI in acetone at 60° see (30).]

[ $\bar{C}$  with  $C_6H_6 + AlCl_3$  gives (yields: 82.5% (9), 69% (31)) *sec.*-butylbenzene (1:7490);  $\bar{C}$  with  $C_6H_6 + Al/Hg$  gives (59.5% yield (32)) *ter*-butylbenzene (1:7460);  $\bar{C}$  with naphthalene +  $AlHg$  gives (48% yield (32)) 1-(*sec.*-butyl)naphthalene.]

[ $\bar{C}$  with acetanilide +  $AlCl_3$  in nethylene dichloride (3:5130) at –5° gives (33) *N*-acetyl-*p*-(*sec.*-butyl)aniline, cryst. from di-isopropyl ether, m.p. 121–122° (33).]

$\bar{C}$  with Mg in dry ether gives (87% yield (34)) *sec.*-BuMgCl (see also below).

⑤ Ethyl-methyl-acetic acid (1:1105): h.p. 176–177°. [From  $\bar{C}$  by conversion to RMgCl and carbonation of the latter with  $CO_2$  (yields: 76–86% (35), 72%) (by adding ether soln. directly to solid  $CO_2$  (36)).]

⑥ Ethyl-methyl-acetic anilide: m.p. 110–111° (37), 108° u.c. (38), 105.5–106.5° u.c. (39). [From  $\bar{C}$  (39) (24) or *sec.*-BuBr (38) by conversion to RMgX and reactn. in dry ether with phenyl isocyanate.] [Note that this prod. does not distinguish  $\bar{C}$  from ethyl chloride (3:7015) or from isopropyl chloride (3:7025) for which the corresp. anilides melt at 101–101.5°; moreover, it is not recommended as distinction from isobutyl chloride (3:7135) for which the corresp. isovalerianilide has m.p. 109–110° u.c. (39).]

⑦ Ethyl-methyl-acetic-*p*-toluidide: m.p. 92.5–93° u.c. (39). [From  $\bar{C}$  by conversion to RMgCl (see above) and reactn. in dry ether with *p*-tolyl isocyanate (39).]

⑧ Ethyl-methyl-acetic  $\alpha$ -naphthalide: m.p. 128–129° u.c. (39). [From  $\bar{C}$  by conversion to RMgCl (see above) and reactn. in dry ether with  $\alpha$ -naphthyl isocyanate (39).] [Note that this prod. does not distinguish  $\bar{C}$  from isobutyl chloride (3:7135) for which the corresp. isovalero- $\alpha$ -naphthalide has m.p. 125–126° u.c. (39).]

— *sec.*-Butyl mercuric chloride (*sec.*-BuHgCl): cryst. from alc., m.p. 30.5° (40). [Reported only by indirect means (40).]

— *S*-(*sec.*-Butyl)isothioureia picrate: m.p. 190° (41). [Not reported from  $\bar{C}$  but obtd. from *sec.*-BuBr (0.2 g.) + thiourea (0.2 g.) refluxed in alc. (2 ml.) for 2 min., then treated with  $PhOH$  (0.2 g.) dislvd. in least possible hot alc. (41).]

— *N*-(*sec.*-Butyl)phthalimide (2-(*N*-phthalimido)butane): m.p. 24.5–25.5° (42). [Not reported from  $\bar{C}$  but obtd. (35% yield (42)) from *sec.*-BuBr with K phthalimide by htg. in s.t. at 210° for 4 hrs.; note that m.p. is too low to be recommended as deriv. for identification.]

— *N*-(*sec.*-Butyl)-3-nitrophthalimide: unreported.

— *N*-(*sec.*-Butyl)tetrachlorophthalimide: unreported.

— *N*-(*sec.*-Butyl)-*o*-sulfobenzoic imide (*N*-(*sec.*-butyl)saccharin): m.p. 81° (43). [Not reported from  $\bar{C}$  but obtd. from *sec.*-BuBr or *sec.*-BuI with sodium saccharin in aq. butylcarbitol (1:6517) on refluxing for 30 min. (43).]

— *N*-(*sec.*-Butyl)-*N*-(*p*-bromobenzenesulfonyl)-*p*-aniside: unreported.

— *p*-(*sec.*-Butoxy)benzoic acid: m.p. 121–123° u.c. (44). [From  $\bar{C}$  (?) or from *sec.*-BuBr with ethyl *p*-hydroxybenzoate (1:1534) in nbs. alc.  $NaOEt$  on refluxing 1 hr. (44).] [Note, however, that this prod. does not distinguish  $\bar{C}$  from the corresp. deriv. of *n*-amyl chloride (3:7460) whose m.p. is 123–124° u.c. (44).]

— *sec.*-Butyl 2,4,6-trifluorophenyl ether: unreported.

— *sec.*-Butyl  $\alpha$ -naphthyl ether: b.p. 293.5° cor. (45). (Corresp. picrate, m.p. 100.5–101.0° cor.; Neut. Eq. calcd. 429, found 427 (45).)

— sec.-Butyl  $\beta$ -naphthyl ether: b.p. 298.5° cor. (45), 298° (46). (Corresp. picrate, m.p. 86.0-86.5° cor (45); 85° (46); Neut. Eq., calcd. 429, found 429 (46).)

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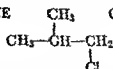
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### 3:7135 1-CHLORO-2-METHYLPROPANE

(isobutyl chloride;

isopropylcarbinyl chloride)



$\text{C}_4\text{H}_9\text{Cl}$

Beil. I - 124

I-(40)

I-(87)

B.P.

M.P.

68.85° at 760 mm. (1) (2) -130.3° (6) (7)  $D_4^{25} = 0.87177$  (1)

68.8-69.2° at 769.2 mm. (3) -131.2° (1) (2)  $D_4^{20} = 0.8810$  (5)

68.5° cor. (4) 0.87733 (1)

68.5° cor. at 756 mm. (5)  $D_4^{15} = 0.86290$  (1)

68.2° (6) (7) (8)

$n_D^{25} = 1.39576$  (1)

$n_D^{20} = 1.39841$  (5)

1.39836 (1)

1.3983 (8)

$n_D^{15} = 1.40096$  (1)

1.40047 (8)

Colorless liquid. — Very spar. sol. aq.; 100 ml. aq. at 12.5° dis. 0.092 g.  $\bar{C}$  (9).

$\bar{C}$  forms with aq. a const.-boilg. mixt. (const. not reported (10)) (use in sepn. from *ter*-butyl alc. (1:6140) (10);  $\bar{C}$  also forms binary azeotropes with many org. compounds; e.g.,  $\bar{C}$  with *EtOH* (1:6130) forms a const.-boilg. mixt., b.p. 61.45° at 760 mm., contg. 72 mole %  $\bar{C}$  (11);  $\bar{C}$  with *propanol-1* (1:6150) forms a const.-boilg. mixt., b.p. 67.7° at 760 mm., contg. 78 wt. %  $\bar{C}$  (12);  $\bar{C}$  with *propanol-2* (1:6135) forms a const.-boilg. mixt., b.p. 64.8° at 760 mm., contg. 83 wt. %  $\bar{C}$  (13);  $\bar{C}$  with *ter*-butyl alc. (1:6140) forms a const.-boilg. mixt., b.p. 65.5° at 760 mm., contg. 83 wt. %  $\bar{C}$  (14);  $\bar{C}$  with *allyl alc.* (1:6145) forms a const.-boilg. mixt., b.p. 67.2° at 760 mm., contg. 93 wt. %  $\bar{C}$  (14);  $\bar{C}$  with *EtOH* (1:6130) + aq. forms a ternary const.-boilg. mixt., b.p. 58.62° at 760 mm. (2 phases), contg. 62.6 mole %  $\bar{C}$  + 19.8 mole % *EtOH* + 17.6 mole % aq. (11).

(For prepn. of  $\bar{C}$  from isobutyl alc. (1:6165) with dry HCl gas in s.t. at 120° for 8 hrs. (3) cf. (23) (gives 94% yield of a mixt. of  $\bar{C}$  + *ter*-butyl chloride (3:7045) from which latter can be removed by 5-hr. shaking with 10% aq. KOH (3) cf. (22); with dry HCl gas at 100° for 10 hrs. (4) or in pres. of pyridine (15) or CdO, ZnCl<sub>2</sub> or other cat. (16); or over Al<sub>2</sub>O<sub>3</sub> at 420° (*ter*-butyl chloride is also formed (17)); with conc. aq. HCl + ZnCl<sub>2</sub> refluxed 1 hr. (15% yield (18) (19)); with PCl<sub>3</sub> + ZnCl<sub>2</sub> (yields: 85% (20), 80% (18), 32% (21)) (note that some *ter*-butyl chloride is formed (21)); with PCl<sub>5</sub> (24) or PCl<sub>5</sub> + ZnCl<sub>2</sub> (76% yield (18)); or with SOCl<sub>2</sub> + pyridine (83% yield (18)) (5), SOCl<sub>2</sub> + dimethylaniline (70% yield (18)), SOCl<sub>2</sub> + diethylaniline (58% yield (18)) (note that use of aniline gives only 19% yield (18)) see indic. refs.)

[For formn. of  $\bar{C}$  from 2-methylpropane (isobutane) with Cl<sub>2</sub> + cat. at 180° (60% yield (25) together with other prods.) (26) see indic. refs.; for formn. of  $\bar{C}$  from isobutylene by cat. addn. of HCl (note "abnormal" addition) see (27).]

[For formn. of  $\bar{C}$  from isobutylamine with NOCl in xylene at -15° (28) or with aqua regia (29) see indic. refs.; from *n*-butyl acetate (1:3145) by pyrolysis with AlCl<sub>3</sub> see (30).]

[For sepn. of  $\bar{C}$  from *ter*-butyl chloride (3:7045) by hydrol. of latter with aq. alk. and extraction of the resultant *ter*-butyl alc. with aq. see (10) (3); for sepn. of  $\bar{C}$  from more reactive alkyl chlorides (such as *ter*-butyl chloride (3:7045), methylal chloride (3:7145), etc.) by esterification of the reactive chlorides by htg. at 125-225° under press. in pres. of Cu with alkali salt of a suitable acid, followed by fractional distn., see (47).]

[ $\bar{C}$  on suitable htg. dec. into isobutylene and HCl; if the process is so conducted that these prods. can react at lower temp. they combine to yield *ter*-butyl chloride (3:7045); e.g.,  $\bar{C}$  passed over pumice at 500° (31), or over clay at 250-300° (32), or over BaCl<sub>2</sub>, ThCl<sub>4</sub>, ThO<sub>2</sub>, kaolin, etc., at 300° (33) (34) (35) (36), or with H<sub>2</sub> over reduced Ni at 270° (35) (36) yields isobutylene + HCl; for execution of this process so as to permit recombination to *ter*-butyl chloride (3:7045) see (37). — Note that  $\bar{C}$  on htg. in s.t. at 306° for 6 hrs. gives (3) 8% *ter*-butyl chloride; for study of the equilibrium in the system  $\bar{C}$  + *ter*-butyl chloride + HCl over range 88-237° see (38).]

[ $\bar{C}$  with Cl<sub>2</sub> yields (39) (26) 1,3-dichloro-2-methylpropane (3:7960) and other prods. —  $\bar{C}$  with Br<sub>2</sub> (1 mole) in pres. of Fe in s.t. at 100° for 6 hrs. gives (40) 1,2-dibromo-2-methylpropane (isobutylene dibromide), b.p. 148° (40).]

[ $\bar{C}$  with aq. soln. or susp. of inorg. bases under press. at 120-350° yields (41) a mixt. contg. isobutyl alc. (1:6165), *ter*-butyl alc. (1:6140), and isobutylene. — For study of rate of hydrolysis of  $\bar{C}$  in 50% alc. in pres. and abs. of dil. H<sub>2</sub>SO<sub>4</sub> see (42). — In connection with hydrolysis of  $\bar{C}$  to isobutyl alc. note that these two form no azeotrope (1).]

[ $\bar{C}$  with Na in liq. NH<sub>3</sub> gives 2-methylpropane (isobutane) (43); but  $\bar{C}$  with NaNH<sub>2</sub> in liq. NH<sub>3</sub> gives isobutylene (43).]

[ $\bar{C}$  with C<sub>6</sub>H<sub>6</sub> + AlCl<sub>3</sub> gives exclusively (44) (45) (46) (21) *ter*-butylbenzene (1:7460).]

$\bar{C}$  with Mg in dry ether in pres. of trace of MeI as cat. gives in 8 hrs. (98.9% yield (48))

corresp. isobutyl MgCl; the ethereal soln. of this RMgCl undergoes the usual reactns. (see also below).

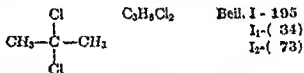
- ③ Isovaleric acid (1:1050) q.v. [From isobutyl MgCl with  $\text{CO}_2$  followed by dil. non-volatile acid and subsequent distn. (49) (yield not reported).]
- ④ Isovaleranilide: m.p. 109–110° u.c. (50). [From isobutyl MgCl (above) with phenyl isocyanate in dry ether (50).] [Note that this derivative does not distinguish  $\bar{\text{C}}$  from isoamyl chloride (3:7365) or 2-chlorobutane (3:7125) q.v.]
- ⑤ Isovalero-*p*-toluidide: m.p. 106–107° u.c. (50). [From isobutyl MgCl (above) with *p*-tolyl isocyanate in dry ether (50).] [Note that this derivative does not distinguish  $\bar{\text{C}}$  from 3-chloropentane (3:7330) q.v., but that it is the best means of distinction from 2-chlorobutane (3:7125).]
- ⑥ Isovalero- $\alpha$ -naphthalide: m.p. 125–126° u.c. (50). [From isobutyl MgCl (above) with  $\alpha$ -naphthyl isocyanate in dry ether (50).] [Note that this derivative does not distinguish  $\bar{\text{C}}$  from 2-chlorobutane (3:7125) q.v.]
- Isobutyl mercuric chloride: unreported.
- *S*-(Isobutyl)isothiourea picrate: m.p. 174° (51). [This prod. has been reported from isobutyl bromide (or iodide) (but not from  $\bar{\text{C}}$ ) by htg. with thiourea in alc. for 2 min., followed by ndln. of alc.  $\text{KOH}$  (51).]
- *N*-(Isobutyl)phthalimide (1-(*N*-phthalimido)-2-methylpropane): lfts. from  $\text{CS}_2$ , m.p. 93° (53). [This prod. has been reported from isobutyl bromide with *K* phthalimide on htg. in s.t. at 210° for 3–4 hrs. (53).]
- *N*-(Isobutyl)-3-nitrophthalimide: unreported.
- *N*-(Isobutyl)tetrachlorophthalimide: unreported.
- *N*-(Isobutyl)-*N*-(*p*-bromobenzenesulfonyl)-*p*-aniside: cryst. from 75% alc., m.p. 78–79° (57). [From  $\bar{\text{C}}$  (?) or the corresp. isobutyl bromide with *N*-(*p*-bromobenzenesulfonyl)-*p*-anisidine in alc.  $\text{KOH}$  after 1 hr. refluxing (57).]
- *N*-(Isobutyl)-*o*-sulfobenzoic imide (*N*-(isobutyl)saccharin: m.p. 75.0° (55). [Not reported from  $\bar{\text{C}}$ , but obtd. from isobutyl bromide or iodide with sodium saccharin in aq. butylcarbitol (1:6517) on refluxing 30 min. (55).]
- *p*-(Isobutoxy)benzoic acid: m.p. 140–141° u.c. (56). [From  $\bar{\text{C}}$  with ethyl *p*-hydroxybenzoate (1:1534) in nbs. alc.  $\text{NaOEt}$  on refluxing 1 hr. (56).] [Note, however, that this prod. does not distinguish  $\bar{\text{C}}$  from isoamyl chloride (3:7365) for which the corresp. *p*-(isoamoxy)benzoic acid has m.p. 141–142° (56).]
- Isobutyl 2,4,6-tri-iodophenyl ether: m.p. 48.0° cor. (52). [This prod. has been obt. from isobutyl bromide (but not  $\bar{\text{C}}$ ) with 2,4,6-tri-iodophenol in alc.  $\text{NaOEt}$  (52).] [Note that it would not distinguish  $\bar{\text{C}}$  from 1-chloropentane (3:7460) or 1-chlorohexane (3:7935).]
- Isobutyl  $\alpha$ -naphthyl ether: b.p. 301.5° cor. (54). (Corresp. picrate, m.p. 104.5–105.5° cor. (54).)
- Isobutyl  $\beta$ -naphthyl ether: b.p. 204.5° cor. (54), m.p. 33.0–33.5° cor. (54). (Corresp. picrate, m.p. 84.0–85.0° cor. (54).)

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3:7140 2,2-DICHLOROPROPANE  
(Isopropylidene (di)chloride;  
"acetone (di)chloride")



B.P.		F.P.	
70.5°	at 760 mm. (1)	-34.6° (8) (9)	$D_4^{25} = 1.084591$ (1)
70.8°	(2)	-34.4° (1)	$D_4^{20} = 1.09151$ (1)
69.7°	(3)	-33.8° (5)	
69.69° cor.	at 760 mm. (4)		$n_D^{20} = 1.41167$ (1)
69.3°	(5)		
68.9-69.3°	(5a)		$D_4^{15} = 1.99843$ (1)
68.86-69.06°	(6)		
68.85-68.87°	at 746 mm. (7)		

$\bar{\text{C}}$  with MeOH (b.p. 61.7°) forms a const.-boilg. mixt., b.p. 55.5°, contg. 79%  $\bar{\text{C}}$ ;  $\bar{\text{C}}$  with EtOH (b.p. 78.3°) forms a const.-boilg. mixt., b.p. 63.2°, contg. 85.5%  $\bar{\text{C}}$  (2).

[For f.p./compn. data on mixts. of  $\bar{\text{C}}$  with methylene (di)chloride (3:5020), with 1,1-dichloroethane (ethylidene (di)chloride) (3:5035), with  $\text{CCl}_4$  (3:5100), or with 1,1,1-trichloroethane (methylchloroform) (3:5085) see (8).]

[For prepn. of  $\bar{\text{C}}$  from acetone (1:5400) with  $\text{PCl}_5$  55% yield (10) (together with 45%

2-chloropropene-1 (3:7020) (10)] see (10) (5) (11) (12); for formn. (25.5% (13)) (together with other products) from propane by vapor-phase chlorination at 400° see (13) (14).]

$\bar{C}$  on hydrolysis by htg. with 8 vols. aq. in s.t. at 160–180° (4), or with HI at 130° (4), or on passing with steam over cat. at 550–550° (15) yields acetone (1:5400). [For behavior of  $\bar{C}$  with boilg. aq. + trace of  $\text{NaHCO}_3$  or with boilg. aq. + Fe see (13).]

$\bar{C}$  with alc. KOH yields (12) (13) (16) (17) 2-chloropropene-1 (3:7020), b.p. 22.3° [ $\bar{C}$  with excess alc. KOH yields (18) propyne-1 (allylene), b.p. -27.5°].

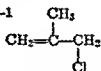
$\bar{C}$  with  $\text{H}_2$  over Ni at 300° (19) or over  $\text{BaCl}_2$  at 380–400° [Beil. I<sub>2</sub>-(73)] gives 2-chloropropene-1 (3:7020), b.p. 22.5°.

3:7140 (1) Timmermans, Delcourt, *J. chim. phys.* 31, 91–92 (1934). (2) Lecat, *Rec. trav. chim.* 46, 242 (1927). (3) Hass, McBee, Weber, *Ind. Eng. Chem.* 28, 338 (1936). (4) Linnemann, *Ann.* 161, 67 (1872). (5) Turkevich, Smyth, *J. Am. Chem. Soc.* 62, 2469 (1940). (5a) Kohlrausch, Köppl, *Monatsh.* 63, 196 (1935). (6) Gross, *Physik. Z.* 32, 589 (1931). (7) Maryott, Hobbs, Gross, *J. Am. Chem. Soc.* 63, 660 (1941). (8) van de Vloed, *Bull. soc. chim. Belg.* 45, 260, 262 (1939). (9) Timmermans, *Bull. soc. chim. Belg.* 25, 300–327 (1911), *Cent.* 1911, II 1015. (10) Henze, Renoll, *J. Am. Chem. Soc.* 59, 2433 (1937).

(11) Friedel, Ladenburg, *Ann.* 142, 315–316 (1867). (12) Friedel, *Ann.* 112, 236 (1859). (13) McBee, Hass, Chao, Welch, Thomas, *Ind. Eng. Chem.* 33, 176–177 (1941). (14) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,073, June 4, 1935, *Cent.* 1936, I 1500. (15) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932, *Cent.* 1932, I 2994. (16) Kahovec, Kohlrausch, *Z. physik. Chem.* B-46, 178 (1940). (17) West, Farnsworth, *Trans. Faraday Soc.* 27, 147 (1931). (18) Friedel, *Ann.* 134, 262–264 (1865). (19) Mailhe, *Bull. soc. chim.* (4) 29, 538 (1921).

### 3:7145 3-CHLORO-2-METHYLPROPENE-1

(Methallyl chloride;  
isobutenyl chloride;  
 $\beta$ -methylallyl chloride;  
 $\gamma$ -chloroisobutylene)



$\text{C}_4\text{H}_7\text{Cl}$  Beil. I - 209

I<sub>1</sub>—  
I<sub>2</sub>—

B.P. [73.74°	(1)]	$D_4^{20} = 0.9175$ (7)	$n_D^{20} = 1.4340$ (7)
71–74°	(2)		
72.2°	(3) (8)		
71.5–72.5°	(4) (5)		
70–71° (6) at 739 mm.	(7)		

[See also 1-chloro-2-methylpropene-1 (3:7120).]

Note that for  $\bar{C}$  the designation methallyl chloride is now preferred (3); great care should be used to avoid confusion of  $\bar{C}$  with the isomeric and very closely related 1-chloro-2-methylpropene-1 = isocrotyl chloride =  $\beta,\beta$ -dimethylvinyl chloride =  $\alpha$ -chloroisobutylene (3:7120); both these compounds are now commercial products in the U.S.A.

Commercial  $\bar{C}$  contains approx. 4% (10) of the isomeric  $\beta,\beta$ -dimethylvinyl chloride (3:7120); owing to the proximity of their boiling points the two isomers are extremely difficult to separate by distillation (8), but owing to the great reactivity of the halogen of  $\bar{C}$  (see amplification below) and the relative unreactivity of the halogen of  $\beta,\beta$ -dimethylvinyl chloride (3:7120) interference from the latter in *metathetical* reactions of comml.  $\bar{C}$  need not be expected.

[For prepn. of  $\bar{C}$  from 2-methylpropene-1 (isobutylene) with  $\text{Cl}_2$  see (3) (2) (5) (9) (other prods. are also formed); for formn. of  $\bar{C}$  as its equilibrium mixt. (10%  $\bar{C}$ ) with  $\beta,\beta$ -dimethylvinyl chloride (3:7120) by actn. of  $\text{H}_2\text{SO}_4$  on latter see (8).]

[For use of  $\bar{C}$  as insecticide see (11) (12); for toxicity studies on beetles see (13); for detn. of  $\bar{C}$  (when used as industrial fumigant) by reaction with ethanolamine in dioxane



(14) or by thermal decomposition (15) see *india. refs.*; for use of  $\bar{C}$  in prepn. of cellulose ethers see (16) (17).]

Reactions involving further substitution of H atoms in  $\bar{C}$ . [ $\bar{C}$  with  $Cl_2$  at room temp. (8) cf. (5) (9) or in pres. of  $NaHCO_3$  soln. at 0° (2) gives (70% yield (8)) a mixt. of approximately equal amounts of 1,3-dichloro-2-methylpropene-1 (3:5590) and 1-chloro-2-(chloromethyl)propene-2 (3:5633) (see also next paragraph).]

Reactions involving the double bond of  $\bar{C}$ . [ $\bar{C}$  with  $Cl_2$  (5) (42) or with  $SO_2Cl_2$  (42) also (see above) adds halogen to the unsaturated linkage yielding (5) (42) 1,2,3-trichloro-2-methylpropane (3:5710), b.p. 163.5–164° at 772 mm. (5).]

[ $\bar{C}$  with  $Br_2$ , however, gives chiefly (93% yield (8)) cf. (5) (9) the expected addition prod., 1-chloro-2,3-dibromo-2-methylpropane [Beil. I-12S], b.p. 57° at 5 mm.,  $D_4^{20} = 1.9168$ ,  $n_D^{20} = 1.5834$  (8).]

[ $\bar{C}$  adds  $HCl$  with considerable difficulty; e.g.,  $\bar{C}$  with equal vol. 12 *N*  $HCl$  at 3°, or  $\bar{C}$  at b.p. treated with  $HCl$  gas for 2 hrs., shows no reaction (3); however,  $\bar{C}$  with equal vol. 12 *N*  $HCl$  shaken for 1½ hrs. at 63° forms 30% of the expected 1,2-dichloro-2-methylpropane (3:7430). —  $\bar{C}$  with dry  $HBr$  gas readily reacts giving (97% yield (8)) 1-chloro-3-bromo-2-methylpropane, b.p. 49° at 15 mm.,  $D_4^{20} = 1.4830$ ,  $n_D^{20} = 1.4816$  (8) (note that this "abnormal" mode of addition of  $HBr$  is presumably attributable to the presence in  $\bar{C}$  of peroxidic material (8)).]

[ $\bar{C}$  with aq.  $HOCl$  below 5° (1) (7) cf. (8), or  $\bar{C}$  with  $Cl_2$ /aq. (8) (18) or even org. hypochlorites (18), gives by addn. of  $HOCl$  to unsatd. linkage 1,3-dichloro-2-methylpropanol-2 (3:5977). —  $\bar{C}$  with aq.  $HOBr$  (from  $Br_2/KBr$  in aq.) at room temp. for 4 hrs. gives 97.5% yield (1) 1-bromo-3-chloro-2-methylpropanol-2, b.p. 84–85° at 20 mm.,  $D_4^{20} = 1.7578$ ,  $n_D^{20} = 1.5171$  (1). —  $\bar{C}$  in ether with aq.  $HgO + I_2$  (HOI) at room temp. for 5–6 hrs. gives (15% yield (1)) 3-chloro-1-iodo-2-methylpropanol-2, b.p. 101–103° at 18 mm.,  $n_D^{20} = 1.547$  (1).]

[ $\bar{C}$  can also add hypochlorite esters; e.g.,  $\bar{C}$  with *ter*-BuOCl (3:7165) in  $MeOH +$  trace *p*-toluenesulfonic acid at 40° for 3–4 hrs. gives (35% yield (6))  $\beta,\beta$ -dichloro-*ter*-butyl methyl ether (1,3-dichloro-2-methoxy-2-methylpropane), b.p. 170° at 748 mm.,  $D_4^{20} = 1.1953$ ,  $n_D^{20} = 1.4595$  (6).]

[ $\bar{C}$  can also undergo cat. hydration of the double bond; e.g.,  $\bar{C}$ , although but slightly sol. in 80%  $H_2SO_4$  at 0°, grad. dissolves on stirring; and after the solution is poured onto ice and the liquid distilled (8) (19) 63% of the original  $\bar{C}$  can be recovered as  $\beta$ -chloro-*ter*-butyl alcohol (isobutylene chlorohydrin) (1-chloro-2-methylpropanol-2) (3:7752). Note that other acids can also be used for this hydration, e.g., 85%  $H_3PO_4$ , 70%  $HNO_3$ , 60%  $HClO_4$ , benzenesulfonic acid, etc., each having its own optimum conditions (8). Note also that in this reaction some 32% of the initial  $\bar{C}$  is not hydrated but is partially isomerized to a mixt. contg. 10%  $\bar{C}$  with 90%  $\beta,\beta$ -dimethylvinyl chloride (3:7120) (see also below) (8).]

[ $\bar{C}$  can also be rearranged to the isomeric isocrotyl chloride; e.g.,  $\bar{C}$  (10 moles) with 80%  $H_2SO_4$  (1 mole) stirred at 40° for 2½ hrs. gives an upper phase which conts. abt. 87% isocrotyl chloride + 7%  $\bar{C}$  + 6% dichlorides and polymers; after washing free from acid, drying, and distilling it yields 85%  $\beta,\beta$ -dimethylvinyl chloride (3:7120) (8) (20).]

[ $\bar{C}$  on sulfonation with dioxann sulfotrioxide in ethylene dichloride gives (21) a complex mixt. of prods.; about 40% of the  $SO_3$  adds to the unsatd. linkage giving a cyclic anhydride of the carboxyl sulfate type, the remainder substituting to yield the three isomeric mono-sulfonic acids of  $\bar{C}$ ; neither polymerization nor disulfonation takes place; for details the original paper (21) should be consulted.]

[For polymerization of  $\bar{C}$  in the pres. of peroxides see (22).]

[ $\bar{C}$  condensed with  $C_6H_6$  in pres. of anhydrous liq.  $HF$  at 0–10° for 20 hrs. as directed



gives (58% yield on CuCN (10)) (27) methallyl cyanide, b.p. 136.2–136.4°,  $D_4^{20} = 0.844$ ,  $n_D^{20} = 1.4202$  (10); note that use of NaCN gives a prod. of somewhat higher b.p., 138.0–139.5° (10), indicating pres. (by rearr.) of some  $\beta,\beta$ -dimethylacrylonitrile, b.p. 140–142°.]

$\bar{C}$  (1 mole) with conc. aq.  $NH_4OH$  (10 moles) at 90° under press. reacts completely within 2 minutes giving (10) (32) mixt. of 56% methallylamine, b.p. 78.8°,  $D_4^{20} = 0.782$ ,  $n_D^{20} = 1.431$  (10) ( $\bar{B}.HCl$ , m.p. 190–191° cor. (41));  $\bar{B}.P.KOH$ , m.p. 202–206° cor. (41)) + 26% di-(methallyl)amine, b.p. 148–149°,  $D_4^{20} = 0.799$ ,  $n_D^{20} = 1.446$  (10), + 8% tri-(methallyl)amine, b.p. 194–195° (32), 83–85° at 15 mm.,  $D_4^{20} = 0.8256$ ,  $n_D^{20} = 1.457$  (10), together with 5% tetra(methallyl)ammonium chloride;  $\bar{C}$  htd. with primary amines behaves in analogous fashion (10) (32).]

$\bar{C}$  with Mg in dry ether under very carefully regulated conditions (using large excess of Mg + ether and slow addn. of  $\bar{C}$ ) gives as high as 90% yield (10) corresp. methallyl  $MgCl$ ; this with acetaldehyde (1:0100) gives (65% yield (10)) the expected secondary alc. 4-methylpenten-4-ol-2, b.p. 129° (10); similarly  $\bar{C}$  with Mg + acetone (1:5400) in dry ether gives (59 mole % yield (10)) 2,4-dimethylpentene-4-ol-2, b.p. 126° (10) accompanied by (37 mole % yield (10)) of the coupling prod. di-methallyl (see next paragraph); note that this coupling reaction is very difficult to suppress.]

$\bar{C}$  with Mg in dry ether (10) (33), or with Na in dry ether (34), gives (yields: 90 mole % (10), 65% (33)) di-methallyl (2,5-dimethylhexadiene-1,5) [Beil. I-259,  $I_1$ -(122),  $I_2$ -(237)], b.p. 114.3° at 760 mm. (10) (33),  $D_4^{20} = 0.7487$  (10), 0.7423 (33),  $n_D^{20} = 1.4293$  (33). — Coupling of  $\bar{C}$  with other reactive alkenyl chlorides can also be effected: e.g.,  $\bar{C}$  with allyl chloride (3:7035) + Mg in dry ether gives (33) 47% yield 2-methylhexadiene-1,5 [Beil. I-257,  $I_1$ -(120)], b.p. 83.1° at 760 mm.,  $D_4^{20} = 0.7198$ ,  $n_D^{20} = 1.4184$  (33), + 30% di-methallyl (see above) + 12% hexadiene-1,5 (biallyl) (1:8045). — For analogous mixed couplings with 2-chloropentene-3 (piperylene hydrochloride) (3:7400) and with 4-chloro-2-methylbutene-2 (isoprene hydrochloride) (3:7465) see (36).]

$\bar{C}$  with  $NaNH_2$  in liq.  $NH_3$  gives (27% yield (35)) 2,5-dimethylhexatriene-1,3,5, b.p. 145° at 747 mm., 90.2° at 200 mm., m.p. -9°,  $n_D^{21} = 1.5150$  (35); note that an intermediate  $\alpha$ -chloro-2,5-dimethylhexadiene, b.p. 33–34° at 5 mm.,  $n_D^{20} = 1.4612$ , has been detected (35).]

$\bar{C}$  reacts normally with other  $RMgX$  compounds: e.g.,  $\bar{C}$  with  $MeMgBr$  in di-isopropyl ether (ord. ether boils too close to prod.) gives (10) 2-methylbutene-1 (1:8210);  $\bar{C}$  with  $n$ -BuMgCl gives (83 mole % yield (10)) (33) 2-methylheptene-1, b.p. 119.3° at 760 mm.,  $D_4^{20} = 0.7206$ ,  $n_D^{20} = 1.4123$  (33) (contaminated with 2-methylheptene-2 formed by rearr. of the former by the inevitable  $MgCl_2$  (33));  $\bar{C}$  with iso-AmMgCl gives (10) 2,6-dimethylheptene-1, b.p. 140–143° (10);  $\bar{C}$  with  $C_6H_5MgBr$  gives (10) methallylbenzene (2-methyl-1-phenylpropene-1), b.p. 175–176° (10).]

[For reactn. of  $\bar{C}$  with diethyl malonate (1:3581) and with various diethyl alkylmalonates see (37); for prepn. of methallyl substituted barbituric acids (37) (4) or thiobarbituric acids (38) see indic. refs.]

— Methallyl acetate [Beil. I-137,  $I_2$ -(150)]; b.p. 124° at 760 mm.,  $D_4^{20} = 0.9239$ ,  $n_D^{20} = 1.4129$  (39). [From  $\bar{C}$  + KOAc at 150° in s.t. (5) (9) cf. (10).] [For data on the formate, propionate, and  $n$ -butyrate see (39).]

— Methallyl benzoate: yel. odorless oil, b.p. 120° at 50 mm. (40). [Prepd. indirectly (40).]

— Methallyl  $p$ -nitrobenzoate: unreported.

— Methallyl 3,5-dinitrobenzoate: unreported.

⑦  $N$ -(Methallyl)phthalimide: white cryst. from MeOH, m.p. 88.5–90° cor. (41). [From  $\bar{C}$  + K phthalimide in s.t. at 150° for 3 hrs. (41).]

- 3:7150 (1) Henze, Murchison, *J. Am. Chem. Soc.* 53, 4077-4079 (1931). (2) Wallace, Henze, *J. Am. Chem. Soc.* 64, 2882 (1942). (3) Baker, *J. Chem. Soc.* 1942, 522.

3:7151 4-CHLOROBUTENE-1  $\text{CH}_2=\text{CH}-\underset{\text{Cl}}{\text{CH}}-\text{CH}_3$   $\text{C}_4\text{H}_7\text{Cl}$  Beil. S.K. 11

B.P. 75.0° at 773 mm. (1)  $D_4^{20} = 0.9211$  (1)  $n_D^{20} = 1.42330$  (1)

Colorless liq. with odor similar to allyl chloride but less strong; insol. aq.

[For prepn. of  $\bar{\text{C}}$  from buten-1-ol-4 (allylcarbinol) (Beil. I-441, I<sub>1</sub>-(226), I<sub>2</sub>-(480)) with  $\text{PCl}_5$  + pyridine (41% yield) see (1).] [ $\bar{\text{C}}$  is not formed (2) (3) during reactn. of butadiene-1,3 with  $\text{HCl}$ .]

3:7151 (1) Juvala, *Ber.* 63, 1993 (1930). (2) Kharasch, Kritchevsky, Mayo, *J. Org. Chem.* 2, 494 (1935). (3) Ganguly, *J. Indian Chem. Soc.* 13, 681, 684 (1936).

3:7153 ACRYLOYL CHLORIDE  $\text{CH}_2=\text{CH}-\underset{\text{Cl}}{\text{C}}=\text{O}$   $\text{C}_3\text{H}_3\text{OCl}$  Beil II - 400  
(Propenoyl chloride)  $\text{II}_1-$   
 $\text{II}_2$ -(388)

B.P. 75-76° (1)  $D_4^{20} = 1.1136$  (13)  $n_D^{20} = 1.4343$  (13)  
74-75° (11)  
74-76° at 760 mm. (13)  $D_4^{20} = 1.14$  (1)  
30-32° at 140 mm. (13)

Colorless mobile strongly lachrymatory liq., fuming in air.

[For prepn. of  $\bar{\text{C}}$  from sodium acrylate with  $\text{POCl}_3$  (yields 80% (11), 60% (1), 27% (12), 22% (9) (2) (3) (4), with  $\text{SOCl}_2$  (19% yield (9)), or from  $\beta$ -chloropropionyl chloride (3:5699) by loss of  $\text{HCl}$  (35% yield (12)) when passed over suitable cat. at 280-300° (5) see indie. refs.; for prepn. of  $\bar{\text{C}}$  from acrylic acid (1:1020) with  $\text{PCl}_5$  (66% yield) see (13).]

[For polymerization of  $\bar{\text{C}}$  by light (10) in pres. of a small amt. of org. base see (6); for polymerization of  $\bar{\text{C}}$  in pres. of u.v. light or by dibenzoyl peroxide see (9).]

[ $\bar{\text{C}}$  with  $\text{MeOH}$  yields (1) methyl  $\beta$ -chloropropionate (3:5765), b.p. 148°;  $\bar{\text{C}}$  with  $\text{EtOH}$  yields (1) ethyl  $\beta$ -chloropropionate (3:8290), b.p. 162°;  $\bar{\text{C}}$  with phenol yields (1) phenyl  $\beta$ -chloropropionate, b.p. 154-157° at 30 mm. (1); note, however, that  $\bar{\text{C}}$  reacting with a large excess of alcs. or phenols and/or in the pres. of acid binding agents such as  $\text{CaCO}_3$  yields (7) esters of acrylic acid.]

[ $\bar{\text{C}}$  with  $\text{Na}$  acrylate yields (1) acrylic anhydride, b.p. 97° at 35 mm. (1).]

$\bar{\text{C}}$  with  $\text{C}_6\text{H}_6$  +  $\text{AlCl}_3$  yields (8) (2) (by Friedel-Crafts reactn. and subsequent ring closure) indanone-1 (1:5144), m.p. 42°.

$\bar{\text{C}}$  in  $\text{CHCl}_3$  treated with  $\text{Br}_2$  in  $\text{CHCl}_3$  yields (1) 2,3-dibromopropionyl chloride, h.p. 191-193°, 97-99° at 37 mm. (1),  $D_4^{20} = 2.181$  (1), which with warm aq. easily hydrolyzes to  $\alpha,\beta$ -dibromopropionic acid, m.p. 64° (1).

$\bar{\text{C}}$  on hydrolysis yields (1) acrylic acid (1:1020) q.v. (for the amide, m.p. 84-85° (11), anilide, and *p*-toluidide corresp. to  $\bar{\text{C}}$  see 1:1020).

3:7153 (1) Moureu, *Ann. chim.* (7) 2, 161-174 (1894). (2) Kohler, *Am. Chem. J.* 42, 380 (1909). (3) van der Burg, *Rec. trav. chim.* 41, 23 (1921). (4) Gilman, Heckert, McCracken, *J. Am. Chem. Soc.* 50, 438 (1928). (5) I. G., *Brit.* 333,079, Aug. 28, 1930; *Cent.* 1930, II 2830; *U.S.* 2,050,752, Aug. 11, 1936; *C.A.* 30, 6762 (1936). (6) Fikenscher (to I. G.), *Ger.* 577,040, May 22, 1933; *Cent.* 1933, II 1250; *C.A.* 27, 3950 (1933). (7) Bauer, Lauth (to Röhm & Haas Co.), *Ger.* 570,955, Feb. 22, 1933; *Cent.* 1933, I 2608. (8) *Ref.* 1, pp. 198-202. (9) Marvel, Levesque, *J. Am. Chem. Soc.* 61, 3244-3246 (1939). (10) Staudinger, Urech, *Helv. Chim. Acta* 12, 1131 (1929).

(11) Jones, Zomlefer, Hawkins, *J. Org. Chem.* 9, 506-507 (1944). (12) Mowry, *J. Am. Chem. Soc.* 66, 371-372 (1944). (13) Rehberg, Dixon, Fisher, *J. Am. Chem. Soc.* 67, 209 (1945).

3:7155 3-CHLORO-3-METHYLBUTYNE-1  $\text{CH}_3$   $\text{C}_4\text{H}_7\text{Cl}$  Bell. S.N. 12  
 (2-Chloro-2-methylbutyne-3)  $\text{HC}\equiv\text{C}-\underset{\text{Cl}}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_3$

B.P.  $76^\circ$  (1)  $D_4^{25} = 0.9061$  (1)  
 $74-76^\circ$  (2)

[For prepn. of  $\hat{\text{C}}$  from 2-methylbutyn-3-ol-2 (dimethyl-ethynyl-carbinol) on shaking as specified (1) (3) with  $\text{HCl} + \text{CuCl}_2 + \text{NH}_4\text{Cl}$ ; if  $\text{Cu}_2\text{Cl}_2$  is used or if reactn. is protracted  $\hat{\text{C}}$  is isomerized (cf. (1)) to 1-chloro-3-methylbutadiene-1,2 (3:7390) q.v.; for reverse conversion of latter to  $\hat{\text{C}}$  (and other products) by hfg. with  $\text{CaCO}_3 + \text{aq.}$  see (3).]

$\hat{\text{C}}$  on hfg. with aq. +  $\text{CaCO}_3$  at  $80^\circ$  gives (2) the precursor 2-methylbutyn-3-ol-2.

$\hat{\text{C}}$  with  $\text{NH}_4\text{OH}/\text{AgNO}_3$  gives (1) a white ppt. [dif. from 1-chloro-3-methylbutadiene-1,3 (3:9200)].

3:7155 (1) Favorskii, Favorskaya, *Compt. rend.* **200**, 839-840 (1935); *Cent.* **1935**, II 1340; *C.A.* **29**, 3651 (1935). (2) Favorskaya, *J. Gen. Chem. (U.S.S.R.)* **9**, 386-395 (1939); *C.A.* **33**, 9281 (1939). (3) Favorskaya, *J. Gen. Chem. (U.S.S.R.)* **9**, 1237-1242 (1939); *C.A.* **34**, 1303 (1940). (4) Hurd (to Commercial Solvents Corp.), U.S. 2,274,611, Feb. 24, 1942; *C.A.* **36**, 4138 (1942).

3:7160 1-CHLOROBUTANE  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$   $\text{C}_4\text{H}_9\text{Cl}$  Bell. I - 118'  
 (n-Butyl chloride;  $\text{Cl}$  I<sub>1</sub>-(38)  
 n-propylcarbinyl chloride) I<sub>2</sub>-(80)

B.P.		F.P.	
$78.0^\circ$	at 760 mm. (1)	$-123.1^\circ$ (1)	$D_4^{25} = 0.88098$ (2)
$78.50^\circ$	at 760 mm. (2)	(2)	
$78.3-78.4^\circ$	at 760 mm. (3)		$D_4^{20} = 0.8806$ (8)
$78.05^\circ$	at 760 mm. (4)		0.88048 (2)
$78.4-78.7^\circ$ u.c.	(5)		0.8859 (5)
$78.4-78.6^\circ$	(6)		0.8845 (12)
$78.1^\circ$	at 760 mm. (7)		0.88387 (11)
$78.0^\circ$	at 762 mm. (8)		(10)
$78^\circ$	(9)		
$77.96^\circ$ cor.	(10)		$D_4^{15} = 0.80107$ (2)
$77.7-77.0^\circ$ at 762.7 mm.	(11)		0.88023 (11)
$77.6-77.7^\circ$ at 743 mm.	(3)		(10)
$77.6^\circ$	at 748 mm. (12)		$n_D^{20} = 1.4023$ (9) (6)
$77.6^\circ$	at 741.3 mm. (13)		1.40223 (8)
$77.5-77.0^\circ$ at 760 mm.	(14)		1.4021 (18)
$77.5^\circ$	(15) (10)		1.40173 (17)
$77.3-77.6^\circ$	(17)		1.40159 (8)
$77.0^\circ$	at 769 mm. (8)		1.40148 (16)
$70-77^\circ$	at 760 mm. (18)		1.40147 (19)

See also Note 1.

Note 1: For further data on b.p. at press. over range 565-760 mm. see (15).

Note 2:  $\hat{\text{C}}$  is very spar. sol. aq.; e.g., 0.066 wt. % at  $12^\circ$  (20).

Binary systems of  $\hat{\text{C}}$  with other org. cpds. For f.p./compn. data on mixts. of  $\hat{\text{C}}$  with *tert*-BuCl (3:7015) see (21); for partial vapor press. (17) or  $n_D^{20}$  (22) of mixts. of  $\hat{\text{C}}$  with *n*-heptane (1:5575) or *n*-BuBr see indic. refs.

$\bar{C}$  forms azeotropes with various other org. cpds.; e.g.,  $\bar{C}$  with MeOH (1:6120) forms a const.-boilg. mixt., b.p. 57.0° at 760 mm., contg. 73 wt. %  $\bar{C}$  (4);  $\bar{C}$  with EtOH (1:6130) forms a const.-boilg. mixt., b.p. 65.7° at 760 mm., contg. 79.7 wt. %  $\bar{C}$  (4);  $\bar{C}$  with *n*-PrOH (1:6150) forms a const.-boilg. mixt., b.p. 74.8° at 760 mm., contg. about 82 wt. %  $\bar{C}$  (4);  $\bar{C}$  with *iso*-PrOH (1:6135) forms a const.-boilg. mixt., b.p. 70.8° at 760 mm., contg. 77 wt. %  $\bar{C}$  (4);  $\bar{C}$  with isobutyl alc. (1:6165) forms a const.-boilg. mixt., b.p. 77.65° at 760 mm., contg. 96 wt. %  $\bar{C}$  (4);  $\bar{C}$  with EtOAc (1:2015) forms a const.-boilg. mixt., b.p. 75.5° at 760 mm., contg. 55 wt. %  $\bar{C}$  (23).

[For prepn. of  $\bar{C}$  from *n*-butyl alc. (1:6180) with dry HCl gas on protracted htg. (11) (13) (24) (25), with conc. aq. HCl + ZnCl<sub>2</sub> (2' moles) (yields: 76-78% (26) (27) (23), 66-72% (30), 64-66% (28), 65% (8)) (31), other metal salts (31) (32), or H<sub>3</sub>PO<sub>4</sub> (33); with PCl<sub>3</sub> + ZnCl<sub>2</sub> (60% yield (30)) (34) or PCl<sub>3</sub> + pyridine (for important study of mechanism see (35) (36)); with PCl<sub>3</sub> + ZnCl<sub>2</sub> (74% yield (30)) cf. (35) (36); with SOCl<sub>2</sub> + pyridine (71% yield (8)) (for important study of mechanism see (37) (36)) see indic. refs.]

[For formn. of  $\bar{C}$  from *n*-butyl HSO<sub>4</sub> with HCl (25); from *n*-butyl MgBr with *p*-toluenesulfonyl chloride (8.7% yield (38)); from *n*-butyl *p*-toluenesulfonate as by-prod. of its reactn. with benzyl MgCl in prepn. of *n*-amylbenzene (39) cf. (40) (41); from *n*-butyl iodide with HgCl<sub>2</sub> in a.t. at 120-120° for 2 hrs. (10); from *n*-butylamine with HNO<sub>2</sub> (5.2%  $\bar{C}$  accompanied by 36.5% butenes + 25% butanol-1 + 13.2% butanol-2 + 2.8% 2-chlorobutane (42)); from *n*-butane with Cl<sub>2</sub> at 400-475° (together with other prods. (3)) see indic. refs.]

[For use as denaturant for alc. see (43) (for detn. of  $\bar{C}$  in denatured alc. see (4)); for use in removal of water from volatile fatty acids see (45); for study of anthelmintic props. see (46).]

Pyrolysis of  $\bar{C}$ . [ $\bar{C}$  at 450-650° without catalyst loses HCl and yields exclusively butene-1 (3) (47); however,  $\bar{C}$  passed at 450° over CaCl<sub>2</sub> cat. gives mixt. contg. 20% butene-1 + 80% *cis* + *trans* isomers of butene-2 (3) (47) (for influence of other cat. cf. (45) (49)).]

Further halogenation of  $\bar{C}$ . [ $\bar{C}$  with Cl<sub>2</sub> under various conditions (50) (51) (52) (53) (54) (5) gives a mixt. of 1,1-dichlorobutane (3:7350), 1,2-dichlorobutane (3:7650), 1,3-dichlorobutane (3:7925), and 1,4-dichlorobutane (3:5835) (together with higher chlorination prods.); note that the chlorination is facilitated by peroxides or by light but inhibited by O<sub>2</sub> (e.g.,  $\bar{C}$  with Cl<sub>2</sub> in absence of air at 0° in dark reacts 7% in 20 hrs. but in pres. of 2 mole % ascaridole 85% in same time or in light 100% in 1 min.; in pres. of 2% O<sub>2</sub> in dark no reactn. occurs in 96 hrs. (18). —  $\bar{C}$  (2.5 moles) with SO<sub>2</sub>Cl<sub>2</sub> (1 mole) + trace dibenzoyl peroxide 3 hrs. under reflux in the dark gives (55) mixt. contg. 25% 1,2-dichlorobutane (3:7680) + 50% 1,3-dichlorobutane (3:7925) + 25% 1,4-dichlorobutane (3:5835). —  $\bar{C}$  (1 mole) with SbCl<sub>5</sub> (1 mole) gives on warming (56) 2,3-dichlorobutane (3:7615).]

$\bar{C}$  with Br<sub>2</sub> in pres. of Fe gives (57) 1,2-dibromobutane [Beil. I-120, I<sub>2</sub>-(83)], b.p. 166°.

Reactions of the halogen atom of  $\bar{C}$ . Note that in  $\bar{C}$  the chlorine atom is much less reactive than that of *sec*-butyl chloride (3:7125) or *ter*-butyl chloride (3:7045).

[For study of hydrolysis of  $\bar{C}$  in pres. and abs. of acid see (53).]

[For study of rate of reactn. of  $\bar{C}$  with LiI, NaI, or KI in acetone see (59) (60).]

[For study of rate of reactn. of  $\bar{C}$  with Na *n*-propylate see (61).]

[ $\bar{C}$  with aniline as directed yields (62) *N*-(*n*-butyl)aniline and/or *N,N*-di-(*n*-butyl)aniline; for analogous study of  $\bar{C}$  with *N*-methylaniline (63), *N*-ethylaniline (63), *o*-toluidine (64), *p*-toluidine (64), *unsym.-m*-xylylidine (65) see indic. refs.]

[ $\bar{C}$  with C<sub>6</sub>H<sub>6</sub> + AlCl<sub>3</sub> gives (66) *sec*-butylbenzene (1:7490) (note isomerization of carbon chain) (for comparison of reactivity of  $\bar{C}$  with other *n*-butyl halides see (67));  $\bar{C}$  with C<sub>6</sub>H<sub>6</sub> + Al/Hg gives both (68) *sec*-butylbenzene (1:7490) and *n*-butylbenzene

(1:7515). —  $\bar{C}$  with toluene +  $AlCl_3$  gives (45% yield (69) of a mixt. of both *m*- and *p*-*sec*-butyltoluenes.]

[ $\bar{C}$  with  $C_6H_6$  in dry liq.  $HCl$  at  $195^\circ$  under press. gives (70) 30% yield *sec*-butylbenzene (1:7490) + 50% di-(*sec*-butyl)benzene; for analogous behavior of  $\bar{C}$  with toluene see (70).]

[ $\bar{C}$  with  $CO$  +  $AlCl_3$  or similar cat. under press. yields (71) acids and ketones.]

Reaction of  $\bar{C}$  to form organometallic cpds. [ $\bar{C}$  with metallic  $Li$  in dry ether under  $N_2$  gives (yields: 75–80% (72), 77% (73), 70–75% (74)) *n*-butyllithium (for study of rate of formn. of *n*-BuLi as compared with *n*-BuBr,  $C_6H_5Br$ ,  $C_6H_5I$  see (85)); this prod. with dry  $CO_2$  in ether at  $0^\circ$  gives (45% yield (75)) di-*n*-butyl ketone (1:5493) or with  $CO_2$  in  $C_6H_6$  at room temp. also (75) tri-*n*-butylcarbinol; for study of relative reactivity of *n*-BuLi as compared with *n*-BuMgBr,  $C_6H_5MgBr$ , etc., see (76); note, however, that full chemistry of *n*-BuLi cannot be discussed here.]

[ $\bar{C}$  with metallic  $Na$  in pet. ether yields (77) *n*-butylsodium; on carbonatioo with  $CO_2$  this prod. gives (77) (78) (79) (80) both *n*-valeric acid (1:1060) and *n*-propylmalonic acid; for study of reactn. of *n*-BuNa with  $C_6H_6$  see (77); note, however, that full chemistry of *n*-BuNa cannot be covered here.]

$\bar{C}$  with  $Mg$  in dry ether gives (yields: 98.5% (81), 91.2% (82) (83), 85% (84)) *n*-BuMgCl; for studies on rate of formn. of *n*-BuMgCl (as compared with  $C_6H_5MgBr$ , or with other *n*-Bu halides, etc.) (85), on effect of rapid addn. of  $\bar{C}$  on yield (83), on effect of concentration of  $\bar{C}$  (84) see indic. refs.; for study of equilibrium composition of ether solns. of *n*-BuMgCl see (86) (87); for study of competitive reaction of mixts. of  $\bar{C}$  with *n*-BuBr and with *n*-BuI in formn. of  $RMgX$  see (88). — For certain important reactions of *n*-BuMgCl see below but note that full chemistry of this cpd. cannot be included here.

[ $\bar{C}$  with  $Mg$  + trace of  $I_2$  but without solvent at  $79$ – $82^\circ$  for 3 hrs. gives (10% yield (89)) *n*-octaoe (1:8655);  $\bar{C}$  +  $Mg$  +  $I_2$  in toluene in similar fashion gives (6% yield (89)) *p*-(*n*-butyl)toluene.]

Ⓐ *n*-Valeric acid (1:1060) q.v. [From  $\bar{C}$  by coconversion to *n*-BuMgCl (see above) and carbonatioo with  $CO_2$  (yields: 72–73% (90), 80% (91)) (note that this prod. may be accompanied by more or less di-*n*-butyl ketone (1:5493) and tri-*n*-butylcarbinol (91)), or by coconversion of  $\bar{C}$  with  $KCN$  to *n*-valeronitrile and hydrolysis of the latter with 67%  $H_2SO_4$  (92) (92).]

Ⓑ *n*-Valeramide: m.p.  $62$ – $63^\circ$  u.c. (93),  $63^\circ$  cor. (94). [From  $\bar{C}$  by conversion to *n*-BuMgCl (see above) and reactn. in dry ether with phenyl isocyanate (93) (42) cf. (93).]

Ⓒ *n*-Valero-*p*-toluidide: m.p.  $72$ – $73^\circ$  u.c. (93). [From  $\bar{C}$  by coconversion to *n*-BuMgCl (see above) and reactn. in dry ether with *p*-tolyl isocyanate (93).] — [Note that this derivative does not afford good distinction from *n*-amyl chloride (3:7460) for which the corresp. *n*-capro-*p*-toluidide has m.p.  $74$ – $75^\circ$  u.c. (93).]

Ⓓ *n*-Valero- $\alpha$ -naphthalide: m.p.  $109$ – $110^\circ$  u.c. (93). [From  $\bar{C}$  by conversion to *n*-BuMgCl (see above) and reactn. in dry ether with  $\alpha$ -naphthyl isocyanate (93).] — [Note that this derivative does not afford good distinction from isoamyl chloride (3:7365) for which the corresp. isocaproic  $\alpha$ -naphthalide has m.p.  $110$ – $111^\circ$  u.c. (93).]

— *n*-Butyl mercuric chloride (*n*-BuHgCl): m.p.  $130^\circ$  cor. (95),  $129^\circ$  (96),  $127.5^\circ$  (98),  $126^\circ$  (96),  $125.5^\circ$  (97),  $125^\circ$  (99). [Prepd. indirectly but should be easily preparable from *n*-BuMgCl +  $HgCl_2$  cf. (98), since it has been similarly prepd. from *n*-BuMgBr (95).]

Ⓔ *S*-(*n*-Butyl)isothioureia picrate: m.p.  $177^\circ$  (100). [From  $\bar{C}$  (1 g.) with thiourea (1 g.) in alc. (10 ml.) on refluxing for 2 hrs., then adding  $PhOH$  (1 g.), htg. until a clear soln. results, then cooling (100).] — [Note that this derivative does not dis-



tinguish  $\bar{C}$  from *n*-propyl chloride (3:7049) for which the corresp. *S*-(*n*-propyl)-isothiourac picrate has m.p. 175° (109), nor from isocamyl chloride (3:7365) for which the corresp. *S*-(isocamyl)-isothiourac picrate has m.p. 173° (103).]

— *N*-(*n*-Butyl)-phthalimide (1-(*N*-phthalimido)butane): cryst. from dil.  $\text{AcOH}$ , m.p. 34° (101), b.p. 311.5° cor. at 738 mm. (102). [Prepd. indirectly from *n*-butylamine (101) (102); direct prepn., e.g., from  $\bar{C} + \text{K phthalimide}$  in pres. of  $\text{KI}$  never reported and m.p. too low to serve as good derivative.]

⑥ *N*-(*n*-Butyl)-3-nitrophthalimide: pr. from  $\text{CS}_2$ , m.p. 71–72° (103). [From  $\bar{C}$  with  $\text{K 3-nitrophthalimide}$  on refluxing for 10 hrs. (103); for photographs of crystals see (104).]

⑦ *N*-(*n*-Butyl)-tetrachlorophthalimide: pl. from alc., m.p. 153–154° (105). [From  $\bar{C}$  with  $\text{K tetrachlorophthalimide}$  by hfg. at 200° for 10 hrs. (105).]

⑧ *N*-(*n*-Butyl)-saccharin: cryst. from dil. alc., m.p. 38° (106). [From  $\bar{C}$  with sodium saccharin in aq. butylcarbitol (1:6317) contg.  $\text{KI}$  on refluxing for 30 min. (106).]

— *N*-(*n*-Butyl)-*N*-(*p*-bromobenzenesulfonyl)-*p*-aniside: cryst. from 75% alc., m.p. 74.5° u.c. (107). [This prod. has not been reported from  $\bar{C}$  but has been obt. from *n*-BuBr with *N*-(*p*-bromobenzenesulfonyl)-*p*-aniside in alc.  $\text{KOH}$  after 1 hr. reflux (107).]

— *p*-(*n*-Butoxy)benzoic acid: m.p. 147–148° (108), changing to a cloudy viscous liq. clearing sharply at 160° (108) cf. (109). [From  $\bar{C}$  with ethyl *p*-hydroxybenzoate (1:1534) in abs. alc.  $\text{NaOEt}$  on refluxing 1 hr. (108)]. — [Note, however, that this prod. does not distinguish  $\bar{C}$  from *n*-propyl chloride for which the corresp. *p*-(*n*-propoxy)benzoic acid has m.p. 143.5–147°; the two prods. do, of course, have slightly different Neut. Eqs.]

— *n*-Butyl 2,4,6-triiodophenyl ether: m.p. 66° cor. (110). [This prod. has not been reported for  $\bar{C}$  itself but has been obt. from *n*-BuBr with 2,4,6-triiodobenzol in abs. alc.  $\text{NaOEt}$  on refluxing for 30 min. (110).]

— *n*-Butyl  $\alpha$ -naphthyl ether: b.p. 308.5° cor. (111), 310° (112) (corresp. picrate, m.p. 83.0° cor., Neut. Eq. 429 (111)).

— *n*-Butyl  $\beta$ -naphthyl ether: b.p. 309.0° cor. (111), 311° (112); m.p. 53.0–53.5° (111) (corresp. picrate, m.p. 67.0–67.5° cor. (111), 67° (115)).

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3:7165 *ter*-BUTYL HYPOCHLORITE  $(\text{CH}_3)_3\text{C}-\text{OCl}$   $\text{C}_4\text{H}_9\text{OCl}$  Beil. I —  
 (Trimethylcarbinyl hypochlorite) I —  
 I<sub>2</sub>-(415)

B.P. 79.6° at 750 mm. (1)  
 77-79° (16)

$D_4^{25} = 0.0583$  (1)

Pale yellow mobile liquid with characteristic irritating odor. —  $\dot{\text{C}}$  violently attacks the eyes and mucous membranes. —  $\dot{\text{C}}$  is relatively stable and if protected from bright light can be kept at ordinary temp. for months with little or no decomposition (1).  $\dot{\text{C}}$  should, however, be handled with care since it is particularly susceptible to photochemical decomposition which may occur with explosive violence (2).

[For prepn. of  $\dot{\text{C}}$  from *ter*-butyl alcohol (1:6140) +  $\text{Cl}_2$  + alk. in pract. quant. yield see (1) (2) (3), 60% yield (16); from *ter*-butyl alc. (1:6140) +  $\text{HOCl}$  in  $\text{CCl}_4$  see (15); for manufacture of  $\dot{\text{C}}$  see (4).] [For use in bleaching of textiles, fruits, etc., see (5) (6) (7).]

[For general survey of reactns. of  $\dot{\text{C}}$  see (8); for study of reactns. of  $\dot{\text{C}}$  with olefins (2) (13) (16) (17) (18) or olefins contg. activating groups (9) (10), with group  $\text{R}_2\text{C}=\text{N.MgX}$  (3); or with Schiff's bases (11) (12) see indic. refs.; for study of  $\dot{\text{C}}$  in Friedel-Crafts reactn. see (14).]

$\dot{\text{C}}$  on sufficient htg. or on exposure to bright sunlight yields (1) acetone (1:5400) + methyl chloride (3:7005). — [For data on stability of  $\dot{\text{C}}$  in aq. or in  $\text{CCl}_4$  see (15).]

$\dot{\text{C}}$  with aq. KI acidified with  $\text{AcOH}$  yields  $\text{I}_2$  (use in detn. of  $\dot{\text{C}}$  (1)).

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3:7170 PROPIONYL CHLORIDE  $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{Cl}$   $\text{C}_4\text{H}_7\text{OCl}$  Beil. II - 243  
 $\text{Cl}$  II<sub>1</sub>-(108)  
 II<sub>1</sub>-(223)

B.P.

F.P.

80° (1) (2) (3)  $-04.0^\circ$  (9)  $D_4^{25} = 1.0508$  (10)  $n_D^{25} = 1.4057$  (1)  
 79-80° (4)  
 78.3° at 766 mm. (5)  $D_4^{25} = 1.0469$  (1)  
 78.3° (6)  
 77.8-78.3° at 723.7 mm. (7)  $D_4^{25} = 1.0646$  (7)  $n_D^{25} = 1.4057$  (7)  
 77-78.5° (8) 1.0565 (5) 1.4038 (5)

[For prepn. of  $\dot{\text{C}}$  from propionic acid (1:1025) with  $\text{PCl}_5$  (77% yield (11)), with  $\text{PCl}_5$  (yields: 67.5% (12), 61% (13), 46% (14)) (15) (16) (note that excess  $\text{PCl}_5$  may not be

used since its b.p.,  $76^\circ$ , is too close to that of  $\bar{C}$  for subsequent sepn.), with  $\text{PCl}_5 + \text{ZnCl}_2$  (91% yield (11)), with  $\text{SOCl}_2$  (4) (note that excess  $\text{SOCl}_2$  may not be used since its b.p.,  $79^\circ$ , is almost identical with that of  $\bar{C}$ ), with benzoyl chloride (3:6240) (yield 84-89% (8)) (17), with sodium chlorosulfonate (18), with benzenesulfonyl chloride +  $\text{NaCl}$  (18), with  $\text{Cl}_2 + \text{S}_2\text{Cl}_2$  in cold (37% yield (19)), with  $\text{SiCl}_4$  in xylene at  $50^\circ$  (50% yield (20)), or with acetonitrile +  $\text{HCl}$  gas at  $0^\circ$  (21) see indie. refs., for prepn. of  $\bar{C}$  from propionic anhydride (1:1100) with phosgene (3:5000) + cat. as directed see (22).]

[ $\bar{C}$  with  $\text{Cl}_2$  (67) or  $\text{CCl}_4$  in sunlight (15) at  $0^\circ$  (23) or in dark at  $40^\circ$  (24) or  $\bar{C}$  with  $\text{SO}_2\text{Cl}_2$  in  $\text{CCl}_4$  in pres. of dibenzoyl peroxide refluxed 4-6 hrs. in dark (25) gives a mixt. contg. mainly  $\beta$ -chloropropionyl chloride (3:5690) accompanied also by  $\alpha$ -chloropropionyl chloride (3:5320) yield: 60%  $\beta$  isomer + 40%  $\alpha$  isomer (25)], note that in the pres. of  $\text{I}_2$  instead of dibenzoyl peroxide only  $\alpha$ -chloropropionyl chloride (3:5320) (45% yield (26)) is produced (25)].

[ $\bar{C}$  with  $\text{Br}_2$  (1 mole) at  $80^\circ$  evolves  $\text{HCl}$  and gives (100% yield (12)) (27) (28)  $\alpha$ -bromopropionyl bromide [Beil. II-256, II<sub>2</sub>-(230)], b.p.  $153-155^\circ$  (12); the reaction is accelerated by light, but the photobromination is retarded by  $\text{O}_2$  (29).]

[ $\bar{C}$  with  $\text{Na}$  propionate on hfg. (14) (30) or  $\bar{C}$  with  $\text{Ag}$  propionate on distn. (31) gives (80% yield (31)) propionic anhydride (1:1100).]

[ $\bar{C}$  passed over heated  $\text{Ni}$  cat. decomposes (32) into ethylene,  $\text{HCl}$  +  $\text{CO}$ , accompanied by smaller amts. methane, hydrogen, and  $\text{CO}_2$ . —  $\bar{C}$  with  $\text{Na}$  in abs. ether is claimed (33) to yield the dipropionate of hexen-3-diol-3,4 [Beil. II-242], b.p.  $108-109^\circ$  at 10 mm. (33).]

[ $\bar{C}$  with *tert*-butyl  $\text{MgBr}$  in dry ether yields (34) not only the expected coupling product *tert*-butyl methyl ketone (pinacolone) (1:5425) but also diethyl ketone (1:5420), propanol-1 (1:6150), and propionic acid (1:1025) accompanied by the propionates of *tert*-butyl-ethyl-carbinol (2,2-dimethylpentanol-3) [Beil. I<sub>1</sub>-(207), I<sub>2</sub>-(446)] and of diethylcarbinol (pentanol-3) (1:6175) (reduction products). —  $\bar{C}$  with  $\text{C}_6\text{H}_5\text{MgBr}$  in ether gives (57% yield (35)) diphenyl-ethyl-carbinol [Beil. VI-687, VI<sub>1</sub>-(331)], m.p.  $95^\circ$ , but  $\bar{C}$  with  $\text{C}_6\text{H}_5\text{MgBr}$  with  $\text{CdCl}_2$  in ether gives (76% yield (36)) ethyl phenyl ketone (propiophenone) (1:5525).]

[ $\bar{C}$  + 2,5-dimethylpyrrole *N*-magnesium bromide in dry ether gives (by rearr.) (37) 3-propionyl-2,5-dimethylpyrrole, colorless cryst. from  $\text{AcOH}$ , m.p.  $102.5^\circ$  (37);  $\bar{C}$  with benzimidazolyl *N*-magnesium bromide in dry ether yields (38) (39) *N*-(propionyl)benzimidazole, m.p.  $125^\circ$  (38) (39) (corresp. picrate, m.p.  $225^\circ$  (38) (39)).]

[ $\bar{C}$  + ethyl acetoacetate +  $\text{Mg}$  in  $\text{C}_6\text{H}_6$  refluxed 2 hrs., treated with aq. gives (36% yield (40)) ethyl  $\alpha$ -propionylacetoacetate, b.p.  $104-106^\circ$  at 12 mm. (40) (isolated as  $\text{Cu}$  enolate, m.p.  $78-79^\circ$ , blue ndlx. from  $\text{MeOH}/\text{aq}$ , violet ndlx. from pet. ether (40)).]

[ $\bar{C}$  with  $\text{FeCl}_3$  (1 mole) on warming evolves  $\text{HCl}$  and gives a prod. which with aq. gives (31% yield (41)) (42) diethyl ketone (1:5420) +  $\text{CO}_2$ , or with alc. yields (43) ethyl  $\alpha$ -propionylpropionate [Beil. III-686, III<sub>2</sub>-(436).]

[ $\bar{C}$  with equal wt.  $\text{ClSO}_3\text{H}$  stood at room temp. 5-10 days, poured into aq. (44), or  $\bar{C}$  with tripropylamine in 1gr. (45) gives (cf. (42)) in small yield 3,5-dimethyl-2-ethyl-6-hydroxypyron-4 [Beil. XVII-453], cryst. from aq. or  $\text{AcOH}$ , m.p.  $151^\circ$  (45).]

[ $\bar{C}$  with olefins or cyclo-olefins (cycloenes) in pres. of cat. adds to unsatn. yielding chloroketones; e.g.,  $\bar{C}$  with ethylene +  $\text{AlCl}_3$  at  $0^\circ$  gives (50% yield (46)) (47)  $\beta$ -chloroethyl ketone (1-chloropentanone-3) (3:9265),  $\bar{C}$  with trimethylethylene (2-methylbutene-2) (1:8220) +  $\text{SnCl}_4$  gives (57% yield (48)) 2-chloro-2,3-dimethylhexanone-4, b.p.  $74-78^\circ$  at 17 mm.,  $D_4^{20} = 0.975$  (48) (note that this prod. on hfg. with dimethylaniline loses  $\text{HCl}$  giving (60% yield (49)) of a mixt. of 2,3-dimethylhexen-2-one-4, b.p.  $164-166^\circ$  at 750 mm.,  $D_4^{20} = 0.872$ ,  $n_D^{20} = 1.4537$  (semicarbazone, m.p.  $209^\circ$  (48)) and 2,3-dimethylhexen-1-one-4, b.p.  $135-162^\circ$  at 750 mm.,  $D_4^{20} = 0.862$ ,  $n_D^{20} = 1.4450$  (semicarbazone, m.p.  $105-110^\circ$  (48));  $\bar{C}$  with cyclohexene (1:8070) +  $\text{SnCl}_4$  gives a prod. which with dimethylaniline loses  $\text{HCl}$

to cyclohexen-1-yl ethyl ketone, b.p. 60° at 10 mm.,  $D_4^{25} = 0.981$ ,  $n_D^{25} = 1.6005$  (oxime, m.p. 79°, semicarbazone, m.p. 195° (40)). — Note, however, that addn. of  $\bar{C}$  to certain types of olefins is followed by spontaneous loss of HCl so that the unsatd. ketone forms the direct product; e.g.,  $\bar{C}$  with isobutylene (2-methylpropene-1) +  $\text{SnCl}_4$  gives (30% yield (48)) 2-methylhexen-2-one-4, b.p. 147–148° at 760 mm.,  $D_4^{25} = 0.859$ ,  $n_D^{25} = 1.4496$  (48) (semicarbazone, m.p. 163° (48)).]

[ $\bar{C}$  with aromatic hydrocarbons + cat. evolves HCl yielding corresp. ketones: e.g.,  $\bar{C}$  with  $\text{C}_6\text{H}_6$  +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives (84% yield (19)) (50) ethyl phenyl ketone (propiophenone) (1:5525);  $\bar{C}$  with toluene (1:7405) +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives (yields: 60% (51), 50% (52)) (53) ethyl *p*-tolyl ketone [Beil. VII-317, VII<sub>1</sub>-(170)], b.p. 238–239°; for analogous reactions of  $\bar{C}$  with *o*-xylene (1:7430) (54), 2-methylnaphthalene (1:7605) (55), anthracene (1:7235) (56), phenanthrene (1:7240) (57), or acenaphthene (1:7225) (58) see indie. refs.; for analogous reactions of  $\bar{C}$  with heterocyclic systems, e.g.,  $\bar{C}$  + 2-nitrofurran +  $\text{TiCl}_4$  (59) or  $\bar{C}$  + thiophene +  $\text{P}_2\text{O}_5$  at 210° for 10–12 hrs. (60), see indie. refs.]

[ $\bar{C}$  with alcs. reacts normally yielding corresp. esters: e.g.,  $\bar{C}$  with MeOH yields methyl propionate (1:3020),  $\bar{C}$  with EtOH yields ethyl propionate (1:3070), etc.; for use of Mg in reaction of  $\bar{C}$  with tertiary alcs., e.g.,  $\bar{C}$  + *ter*-butyl alc. (1:6140) + Mg giving (68% yield (61)) *ter*-butyl propionate, b.p. 115–116.5° (61), or  $\bar{C}$  + *ter*-amyl alc. (1:6160) + Mg giving (75% yield (61)) *ter*-amyl propionate, b.p. 153–156° at 710 mm. (61), see indie. refs.]

[ $\bar{C}$  with phenols gives the corresp. phenol esters: e.g.,  $\bar{C}$  with phenol gives (62) phenyl propionate (1:3696), etc.; note, however, that these phenol esters on htg. with  $\text{AlCl}_3$  in appropriate solvents, especially nitrobenzene, undergo the Fries rearr. yielding *o*- and *p*-propiophenols; this complete sequence is often carried through without isolation of the intermediate ester, e.g., for  $\bar{C}$  + phenol +  $\text{AlCl}_3$  giving directly *o*-hydroxypropiophenone [Beil. VIII-102, VIII<sub>1</sub>-(547)] (50% yield) and *p*-hydroxypropiophenone [Beil. VIII-102 (25% yield) see (63); for key refs. on direct rearr. of phenyl propionate to these products see (64) (65); scores of analogous cases with other phenols or their ethers cannot be included here.]

[ $\bar{C}$  with certain hydroxy-azo-compounds in dry ether yields addn. cpds. usually (but not always) of 1:1 type: e.g.,  $\bar{C}$  with *p*-hydroxy-azobenzene [Beil. XVI-96, XVI<sub>1</sub>-(233)], m.p. 152°, in dry ether on stdg. at room temp. ppts. 1:1 cpd., m.p. 162° (66); for numerous analogous cases using homologous hydroxy-azo cpds. see (66).]

$\bar{C}$  hydrolyzes with aq. yielding propionic acid (1:1025); for the amide, anilide, *p*-toluidide, and other derivs. corresp. to  $\bar{C}$  see under propionic acid (1:1025).

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**3:7175 1-CHLOROBUTYNE-2**  $\text{CH}_3\text{—C}\equiv\text{C—CH}_2\text{Cl}$   $\text{C}_4\text{H}_5\text{Cl}$  **Beil. S.N. 12**  
 ( $\gamma$ -Methylpropargyl chloride)

**B.P. 81-84° (1)**

Pale yel. oil.

[For prepn. of  $\bar{C}$  (44% yield) from butyn-2-ol-1 +  $\text{PCl}_5$  in ether see (1).]

$\bar{C}$  in ether/acetone soln. on treatment with  $\text{K}_2\text{CO}_3$  + phenol gives (57% yield)  $\gamma$ -methylpropargyl phenyl ether, b.p. 123-126° at 25 mm.,  $n_D^{20} = 1.3894$  (1).

**3:7175 (1)** Hurd, Cohen, *J. Am. Chem. Soc.* 53, 1074-1075 (1931).

**3:7195 CHLOROMETHYLETHYL ETHER**  $\text{C}_2\text{H}_5\text{OCl}$  **Beil. I - 581**  
 $\text{ClCH}_2\text{O.C}_2\text{H}_5$  **I<sub>1</sub>-(304)**  
**I<sub>2</sub>-(645)**

B.P. 83° at 763.1 mm. (1)	$D_4^{20} = 1.0263$ (3)	$n_D^{20} = 1.40308$ (1)
82° (2)	1.0127 (1)	
81-82° (3)	$D_4^{15} = 1.0188$ (1)	$n_D^{12} = 1.0282$ (3) (7)
80° (4)		
79-80° (5) (6)		

$\bar{C}$  undergoes some decompn. at b.p.

[For prepn from ethyl alc. (1:6130) + trioxymethylene (1:0050) + dry  $\text{HCl}$  see (3) (1); from ethyl alc. + formalin +  $\text{HCl}$  (42-41% yield (6)) see (6).]

$\bar{C}$  on shaking with aq. readily hydrolyzes yielding formaldehyde (1:0145), ethyl alc. (1:6130), +  $\text{HCl}$ .

to cyclohexen-1-yl ethyl ketone, b.p. 90° at 10 mm.,  $D_4^{15.5} = 0.881$ ,  $n_D^{15.5} = 1.5005$  (crime, m.p. 79°, semicarbazone, m.p. 195° (49)). — Note, however, that addn. of  $\bar{C}$  to certain types of olefins is followed by spontaneous loss of HCl so that the unsatd. ketone forms the direct product; e.g.,  $\bar{C}$  with isobutylene (2-methylpropene-1) +  $\text{SnCl}_4$  gives (50% yield (48)) 2-methylhexen-2-one-4, b.p. 147–148° at 760 mm.,  $D_4^{15} = 0.839$ ,  $n_D^{15} = 1.4496$  (48) (semicarbazone, m.p. 163° (48)).]

[ $\bar{C}$  with aromatic hydrocarbons + cat. evolves HCl yielding corresp. ketones: e.g.,  $\bar{C}$  with  $\text{C}_6\text{H}_6$  +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives (84% yield (19)) (50) ethyl phenyl ketone (propiophenone) (1:5525);  $\bar{C}$  with toluene (1:7405) +  $\text{AlCl}_3$  in  $\text{CS}_2$  gives (yields: 60% (51), 50% (52)) (53) ethyl p-tolyl ketone [Beil. VII-317, VII<sub>r</sub>-(170)], b.p. 238–239°; for analogous reactions of  $\bar{C}$  with o-xylene (1:7430) (54), 2-methylnaphthalene (1:7605) (55), anthracene (1:7233) (56), phenanthrene (1:7240) (57), or acenaphthene (1:7225) (58) see indic. refs.; for analogous reactions of  $\bar{C}$  with heterocyclic systems, e.g.,  $\bar{C}$  + 2-nitrofurran +  $\text{TiCl}_4$  (59) or  $\bar{C}$  + thiophene +  $\text{P}_2\text{O}_5$  at 210° for 10–12 hrs. (60), see indic. refs.]

[ $\bar{C}$  with alic. reacts normally yielding corresp. esters: e.g.,  $\bar{C}$  with MeOH yields methyl propionate (1:3020),  $\bar{C}$  with EtOH yields ethyl propionate (1:3070), etc.; for use of Mg in reaction of  $\bar{C}$  with tertiary alic., e.g.,  $\bar{C}$  + *tert*-butyl alc. (1:6140) + Mg giving (63% yield (61)) *tert*-butyl propionate, b.p. 115–116.5° (61), or  $\bar{C}$  + *tert*-amyl alc. (1:6160) + Mg giving (75% yield (61)) *tert*-amyl propionate, b.p. 153–156° at 710 mm. (61), see indic. refs.]

[ $\bar{C}$  with phenols gives the corresp. phenol esters: e.g.,  $\bar{C}$  with phenol gives (62) phenyl propionate (1:3096), etc.; note, however, that these phenol esters on htg. with  $\text{AlCl}_3$  in appropriate solvents, especially nitrobenzene, undergo the Fries rearr. yielding o- and p-propiophenols; this complete sequence is often carried through without isolation of the intermediate ester, e.g., for  $\bar{C}$  + phenol +  $\text{AlCl}_3$  giving directly o-hydroxypropiophenone [Beil. VIII-102, VIII<sub>r</sub>-(547)] (50% yield) and p-hydroxypropiophenone [Beil. VIII-102 (25% yield) see (63); for key refs. on direct rearr. of phenyl propionate to these products see (64) (65); scores of analogous cases with other phenols or their ethers cannot be included here.]

[ $\bar{C}$  with certain hydroxy-aro-compounds in dry ether yields addn. cpds. usually (but not always) of 1:1 type: e.g.,  $\bar{C}$  with p-hydroxy-arobenzene [Beil. XVI-96, XVI<sub>r</sub>-(233)], m.p. 152°, in dry ether on stdg. at room temp. ppts. 1:1 cpd., m.p. 162° (66); for numerous analogous cases using homologous hydroxy-aro cpds. see (66).]

$\bar{C}$  hydrolyzes with aq. yielding propionic acid (1:1025); for the amide, anilide, p-toluidide, and other derivs. corresp. to  $\bar{C}$  see under propionic acid (1:1025).

- 3:7170 (1) Kochl, Wesake, *J. Am. Chem. Soc.* 59, 1418 (1937). (2) John, Boets, *J. prakt. Chem.* (2) 143, 344 (1935). (3) Sestini, *Bull. soc. chim.* (2) 11, 470 (1959). (4) Barden, *Bull. soc. chim.* (4) 49, 1427 (1931). (5) Martin, Partington, *J. Chem. Soc.* 1936, 162. (6) Kohlrausch, Fongratz, *Z. physik. Chem.* B-27, 381 (1933). (7) Brühl, *Ann.* 203, 14–15 (1880). (8) Brown, *J. Am. Chem. Soc.* 60, 1326 (1938). (9) Timmermans, Malsar, *Bull. soc. chim. Belg.* 30, 216 (1921). (10) Walden, *Z. physik. Chem.* 55, 222 (1906). (11) Clark, *Bell. Trans. Roy. Soc. Can.* (3) 21, III 97–103 (1933). (12) Fourneau, Nicolitch, *Bull. soc. chim.* (4) 43, 1236–1238 (1928). (13) Fierz-David, Kuster, *Helv. Chim. Acta* 22, 89 (1939). (14) Linemann, *Ann.* 148, 255–257 (1868). (15) Michael, *Ber.* 34, 4046–4051 (1901). (16) Aschan, *Ber.* 31, 2346 (1898). (17) Chem. Fabrik vorm. Weiler-ter-Meer, *Ger.* 350,030, March 11, 1922; *Cent.* 1922, IV 153. (18) Henle, Schirm (to M. L. B.), *Ger.* 397,311, July 1, 1924; *French* 568,831, March 22, 1924; *Cent.* 1924, II 1401–1402. (19) Read, *J. Am. Chem. Soc.* 44, 1731 (1922). (20) Montonna, *J. Am. Chem. Soc.* 49, 2115 (1927). (21) Colson, *Compt. rend.* 121, 1155 (1895). (22) Stellmann, *French* 753,073, Aug. 1, 1935; *Cent.* 1935, II 8301. (23) Kuster, *Z. physik. Chem.* 130, 9–10 (1923). (24) Hertel, Becker, *Z. physik. Chem.* B-27, 310–311 (1934). (25) Kharasch, Brown, *J. Am. Chem. Soc.* 62, 925–929 (1940). (26) Wolfenstein, Rolle, *Ber.* 41, 735 (1908). (27) Aschan, *Ber.* 45, 1913–1919 (1912).

- (24) Aschan, *Ber.* 46, 2162 (1913). (25) Kharasch, Hobbs, *J. Org. Chem.* 6, 709-712 (1941). (30) Anderlini, *Gazz. chim. ital.* 25, II 132-133 (1895). (31) Whittier, *J. Chem. Soc.* 1926, 1462. (32) Mailhe, *Compt. rend.* 180, 1112 (1925). (33) Anderlini, *Gazz. chim. ital.* 25, II 45, 129 (1895). (34) Petrov, Moslova, *J. Gen. Chem. (U.S.S.R.)* 10, 973-976 (1940), *C.A.* 35, 2167 (1941). (35) Gilman, Fothergill, Parker, *Rec. trav. chim.* 69, 750 (1929). (36) Gilman, Nelson, *Rec. trav. chim.* 65, 528-530 (1936). (37) Oddo, Acuto, *Gazz. chim. ital.* 65, 1033 (1935); *Cent.* 1936, I 3532, *C.A.* 30, 4557 (1936). (38) Oddo, Ruffa, *Gazz. chim. ital.* 67, 541 (1937); *Cent.* 1938, I 1541, *C.A.* 32, 1697 (1938). (39) Oddo, Ingraffia, *Gazz. chim. ital.* 67, 1036 (1937); *Cent.* 1937, I 2913. (40) Spassow, *Ber.* 70, 2353-2354 (1937). (41) Hamonet, *Bull. soc. chim.* (2) 50, 356-357 (1888). (42) Wedekind, *Ann.* 323, 250, 254 (1902). (43) Hamonet, *Bull. soc. chim.* (3) 2, 335-335 (1889). (44) Krajinovic, *Ber.* 62, 579-581 (1929). (45) Wedekind, Hausermann, *Ber.* 41, 2299-2302 (1908). (46) Kenner, Kistham, *Ber.* 69, 17 (1936). (47) Schoeller, Zöllner (to Schering-Kahlbaum A.G.), *U.S.* 1,737-203, Nov. 26, 1929, *Cent.* 1930, II 1133, *Brit.* 252,412, Feb. 15, 1928, *Cent.* 1929, I 143. (48) Colonge, Mostafavi, *Bull. soc. chim.* (5) 6, 335-342, 342-351 (1939). (49) Colonge, Deroux, *Bull. soc. chim.* (5) 7, 459-468 (1941). (50) Pampel, Schmidt, *Ber.* 19, 2896 (1886). (51) Sanchez, *Bull. soc. chim.* (4) 45, 284 (1929). (52) Willgerodt, Hambrecht, *J. prakt. Chem.* (2) 81, 76 (1910). (53) Klages, *Ber.* 35, 2252 (1902). (54) von Auwers, Ziegler, *Ann.* 425, 260 (1921). (55) Haworth, Bolam, *J. Chem. Soc.* 1932, 2219. (56) I G., *Brit.* 259,585, May 24, 1924; *Cent.* 1928, II 1036. (57) Bachmann, Struve, *J. Am. Chem. Soc.* 58, 1659 (1936). (58) Dolewski, Moraw, *Bocznik Chem.* 11, 415-425 (1931), *Cent.* 1931, II 670, *C.A.* 26, 2975 (1932). (59) Gilman, Burtner, Galloway, Turck, *J. Am. Chem. Soc.* 57, 908 (1935). (60) Steinkopf, Schubart, *Ann.* 424, 8-9 (1921). (61) Spassow, *Ber.* 70, 1924-1929 (1937). (62) Perkin, *J. Chem. Soc.* 55, 547-548 (1889). (63) Torres, Amargos, *Anales soc. españ. fis. quim.* 21, 37-47 (1933), *Cent.* 1933, II 372, *C.A.* 27, 1624 (1933). (64) Miller, Hartung, *Org. Syntheses*, Coll. Vol. 2 (1st ed.), 543-545 (1943); 13, 99-92 (1943). (65) von Auwers, Pöls, *Noll, Ann.* 535, 228-230 (1934). (66) Fischer, Taurinisch, *Ber.* 64, 236-239 (1931). (67) Schmidt, Schlotter (to I G.) *Ger.* 734,394, July 18, 1943; *C.A.* 34, 3992 (1941).

3:7175 1-CHLOROBUTYNE-2  $\text{CH}_3\text{—C}\equiv\text{C—CH}_2\text{Cl}$   $\text{C}_4\text{H}_7\text{Cl}$  *Beil. S.N. 12*  
( $\gamma$ -Methylpropargyl chloride)

B.P. 81-81° (1)

Pale yel. oil.

[For prepn. of  $\bar{C}$  (41% yield) from butyn-2-ol-1 +  $\text{PCl}_5$  in ether see (1)]

$\bar{C}$  in ether/acetone soln. on treatment with  $\text{K}_2\text{CO}_3$  + phenol gives (57% yield)  $\gamma$ -methylpropargyl phenyl ether, b.p. 123-126° at 25 mm,  $n_D^{20} = 1.3591$  (1).

3:7175 (1) Hurd, Cohen, *J. Am. Chem. Soc.* 53, 1974-1975 (1931)

3:7195 CHLOROMETHYL ETHYL ETHER  $\text{C}_2\text{H}_5\text{OCl}$  *Beil. I - 581*  
 $\text{ClCH}_2\text{O C}_2\text{H}_5$  *I<sub>1</sub>-(301)*  
*I<sub>2</sub>-(615)*

B.P. 53° at 763.1 mm. (1)	$D_4^{20} = 1.0263$ (3)	$n_D^{20} = 1.40398$ (1)
82° (2)	1.0127 (1)	
81-82° (3)	$D_4^{15} = 1.0188$ (1)	$n_D^{15} = 1.0282$ (3) (?)
80° (4)		
79-80° (5) (6)		

$\bar{C}$  undergoes some decompn. at b.p.

[For prepn. from ethyl alc. (1:6130) + trioxymethylene (1:0050) + dry  $\text{HCl}$  see (1) (1); from ethyl alc. + formalin +  $\text{HCl}$  (42-41% yield) (5)] see (6)]

$\bar{C}$  on slaking with aq. readily hydrolyzes yielding formaldehyde (1:0145), ethyl alc. (1:6130), +  $\text{HCl}$ .



3:7195 (1) Karvonen, *Ann. Acad. Sci. Fennicae*, 3-A, No. 7, 1-103 (1912); *Cent.* 1912, II 1269; *C.A.* 14, 2175 (1920). (2) Litterscheid, *Ann.* 330, 123 (1904). (3) Farren, Fife, Clark, Garland, *J. Am. Chem. Soc.* 47, 2421 (1925). (4) Wedekind, *Ber.* 36, 1385 (1903). (5) de Gaspari, *Gazz. chim. ital.* 27, II 297 (1897). (6) Foran, *J. Soc. Chem. Ind.* 44, 173-174T (1925).

3:7200 1-CHLORO-2,2-DIMETHYLPROPANE  $\text{CH}_3$   $\text{C}_4\text{H}_9\text{Cl}$  *Beil.* I - 141  
(Neopentyl chloride;  
*ter*-butylcarbinyl chloride)  $\text{CH}_3-\text{C}-\text{CH}_2\text{Cl}$  I - (50)  
 $\text{CH}_3$  I -

B.P.	F.P.		
84.4° at 760 mm. (1)	-20° (1) (4)	$D_4^{20} = 0.866$ (1)	$n_D^{20} = 1.4042$ (1)
83.9° at 760 mm. (1)		0.865 (3)	1.4043 (3)
83.5° at 740 mm. (1)			
83.3-84.5° (2)			
82-83.5° at 734 mm. (3)			
24° at 80 mm. (4)			

[For prepn. of  $\bar{\text{C}}$  (30% yield (3)) from neopentane (tetramethylmethane) (1:8499) by chlorination in light at 0° see (4) (3) (1). —  $\bar{\text{C}}$  cannot (1) (5) (contrary to earlier claims (6)) be prepared from neopentyl alc. (*ter*-butylcarbinol) (1:5812) even with  $\text{SOCl}_2 + \text{pyridine}$  (13).]

$\bar{\text{C}}$  is stable for long periods of time even at 200° (1). —  $\bar{\text{C}}$  is extraordinarily unreactive giving none of the ordinary alkyl halide reactns. except the formn. of the corresponding Grignard reagent.

$\bar{\text{C}}$  in dil. ether soln. reacts slowly with Mg giving (1) (90% yield (8)) neopentyl  $\text{MgCl}$ . [For reactn. of  $\text{R.MgCl}$  with  $\text{CO}_2$  see (12).]

[For reactns. of  $\bar{\text{C}}$  with  $\text{C}_6\text{H}_6 + \text{AlCl}_3$  (2), or with metallic Na (10), or with  $\text{NaPr}$  (11) see indic. refs.]

$\bar{\text{C}}$  is unchanged after htg. 20 hrs. at 100° with alc. KOH (1) or htg. with  $\text{CuCN}$  at 90° in a s.t. for 200 hrs. (1) or after treatment with KI in acetone (1) or after 6 hrs. refluxing with 6% Na/Hg (11).

① *ter*-Butylacetanilide ( $\beta,\beta$ -dimethyl-*n*-butyranilide): m.p. 131° (1), 130-131° (3), 129-130° (3). [From  $\text{R.MgCl}$  by reactn. with phenyl isocyanate (1).]

② Neopentyl mercuric chloride: m.p. 117-118° (3), 116.5-117° (1). [From  $\text{R.MgCl}$  with  $\text{HgCl}_2$  (1) (3) in dry ether (90% yield (3)).] [For reactn. of  $\text{R.MgCl}$  with di-*p*-tolylmercury giving di-neopentylmercury, b.p. 67-69° at 3 mm., m.p. 31-33°, see (9).] [For reactn. of  $\text{RHgCl}$  with KBr giving 82% yield neopentyl bromide, b.p. 104.8° at 732 mm., or with  $\text{I}_2$  giving 92% yield neopentyl iodide, b.p. 70° at 100 mm., see (3).]

3:7200 (1) Whitmore, Fleming, *J. Am. Chem. Soc.* 55, 4161-4162 (1933). (2) Pines, Schmerling, Ipatieff, *J. Am. Chem. Soc.* 62, 2901-2902 (1939). (3) Whitmore, Wittle, Popkin, *J. Am. Chem. Soc.* 61, 1585-1590 (1939). (4) Fleming, Whitmore, *J. Am. Chem. Soc.* 54, 3460-3461 (1932). (5) Whitmore, Rothrock, *J. Am. Chem. Soc.* 54, 3431-3435 (1932). (6) Tissier, *Ann. chim.* (6) 29, 344 (1893). (7) Richard, *Ann. chim.* (8) 21, 341-342 (1910). (8) Whitmore, Wittle, Harri-man, *J. Am. Chem. Soc.* 61, 1585-1586 (1939). (9) Whitmore, Rohrmann, *J. Am. Chem. Soc.* 61, 1591-1592 (1939). (10) Whitmore, Popkin, Bernstein, Wilkins, *J. Am. Chem. Soc.* 63, 124-127 (1941).

(11) Whitmore, Look, *J. Am. Chem. Soc.* 64, 1783-1785 (1942). (12) Bush, *J. Am. Chem. Soc.* 61, 965 (1939). (13) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2534 (1938).

3:7205	1-CHLOROBUTENE-2	$\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}_2\text{Cl}$	$\text{C}_4\text{H}_7\text{Cl}$	Beil. I - 205
	(Crotonyl chloride,			$\text{I}_1$ —
	$\alpha$ -chloro- $\beta$ -butylene, $\gamma$ -methylallyl chloride)			$\text{I}_2$ -(176)
B.P. 84°	at 750 mm. (1)	$D_4^{20} = 0.9340$ (3)	$n_D^{20} = 1.4350$ (1) (2) (17)	
84-85°	(2)	0.9316 (7)	1.4351 (5)	
83.8°	(3)		1.4352 (7)	
83°	(7)		1.4356 (3)	
80°	(4)		1.4359 (6)	
45.6-45.7°	at 191 mm. (5)			
43.7-44.0°	at 177 mm. (5)			
-2°	at 18 mm. (6)			

Because of the close interrelationship of  $\tilde{\text{C}}$  with the isomeric 3-chlorobutene-1 (3:7090) some confusion exists regarding the nomenclature. The compound here described (1-chlorobutene-2) is by some authors designated as crotyl chloride; this name, however, is better reserved for the equilibrium mixture of 1-chlorobutene-2 and 3-chlorobutene-1 as indicated by (7).

Pure  $\tilde{\text{C}}$  (in the absence of catalysts) is quite stable (1) and may be kept at room temperature as long as a year (5) without significant increase in  $n_D^{20}$ . However, in the presence of  $\text{FeCl}_3$ ,  $\text{HCl}$ , or  $\text{CuCl}_2 + \text{HCl}$ ,  $\tilde{\text{C}}$  is in part isomerized to 3-chlorobutene-1 and an equilibrium mixt. is formed. The composition of this equilibrium mixt. depends upon the temperature, catalyst, and other factors. E.g., with  $\text{FeCl}_3$  the equilibrium mixt. conts. 50%  $\tilde{\text{C}}$ ; with 1 mole  $\text{HCl}$  it conts. 75%  $\tilde{\text{C}}$ . Although the two compounds can easily be separated by careful fractional distillation (5) yet consideration must always be given to the possible formation during chem. reaction of the derivatives of the other isomer. The refractive index of mixts. of 1-chlorobutene-2 and 3-chlorobutene-1 is a linear function of the composition (1). Although *cis* and *trans* stereoisomers of  $\tilde{\text{C}}$  are possible, no record of their isolation has been published.

[For the prepn. of a mixt. of  $\tilde{\text{C}}$  + 3-chlorobutene-1 from butadiene-1,3 +  $\text{HCl}$  see (1) (7) (8) (9); for prepn. of  $\tilde{\text{C}}$  from crotonyl alcohol with  $\text{PCl}_3$  + pyridine see (3) (5), with  $\text{HCl}$  +  $\text{Cu}_2\text{Cl}_2$  see (1), with conc.  $\text{HCl}$  see (5) ]

$\tilde{\text{C}}$  passed over soda-lime in an iron furnace at 530-550° yields (11) butadiene-1,3. [Use in prepn. of 1,2,3,4-tetrabromobutane (11).]

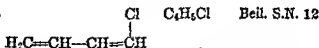
[For study of reactivity of  $\tilde{\text{C}}$  with  $\text{KI}$  soln. at 20° or  $\text{NaOEt}$  soln. at 20° and 50° see (3); for reaction with  $\text{Mg}$ ,  $\text{Zn}$ , etc., see (12); for use in formn. of cellulose ethers see (13); for study of hydrolysis of  $\tilde{\text{C}}$  under various conditions see (16); for behavior of  $\tilde{\text{C}}$  with cuprous cyanide see (17) ]

— Crotonyl 3,5-dinitrobenzoate: cryst. from alc., m.p. 54° (9). [This cpd. has never been reported from  $\tilde{\text{C}}$  but only (cf., however (15)) from the corresp. bromide via reaction with silver 3,5-dinitrobenzoate in ether (9); it is possible that the material of m.p. 54° represents a mixt. of the two esters corresponding to crotonyl bromide and the isomeric 3-bromobutene-1 since from the former a 3,5-dinitrobenzoate, m.p. 51°, 50-51° (15), and from the latter a 3,5-dinitrobenzoate, m.p. 59°, have been reported (14).]

3:7205 (1) Kharsach, Kritchevsky, Mayo, *J. Org. Chem.* 2, 494-496 (1938). (2) Baudrenghien, *Bull. soc. chim. Belg.* 31, 168 (1922) (3) Tamele, Ott, Marple, Hearne, *Ind. Eng. Chem.* 33, 118-119 (1941). (4) Ganguly, *J. Indian Chem. Soc.* 13, 584 (1936). (5) Roberts, Young, Winstein, *J. Am. Chem. Soc.* 64, 2163 (1942) (6) Böhme, *Ber.* 71, 2378-2379 (1938). (7) Henne, Chanan, Turk, *J. Am. Chem. Soc.* 63, 3474-3476 (1941) (8) Dykstra (to du Pont), U.S. 2,123,504, July 12, 1938; *Chem. Abstr.* 1939, II 2840, C.A. 32, 6666 (1938). (9) Voigt, *J. prakt. Chem.* (2) 151, 310 (1938). (10) Charon, *Ann. chim.* (7) 17, 228-230 (1899).

(11) Jacobson, *J. Am. Chem. Soc.* **54**, 1546 (1932). (12) Young, Eisner, *J. Am. Chem. Soc.* **63**, 2113-2115 (1941). (13) Hahn (to du Pont), U.S. 2,082,797, June 8, 1937; *Cent.* 1937, II 3838; *C.A.* **31**, 5577 (1937).  
 Kenner, *J. Chem. Soc.* 1935,  
 (17) Lane, Fentress, Sherwood

## 3:7210 1-CHLOROBUTADIENE-1,3



B.P. 85° (1)  
 68° (2)

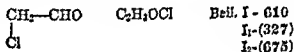
$D_{20}^{25} = 0.9601$  (2)  $n_D^{20} = 1.470$  (3)  
 $n_D^{25} = 1.4733$  (2)

[For prepn. of  $\bar{C}$  from either 1,2-dichlorobutene-3 (3:5350) or 1,4-dichlorobutene-2 (3:5725) by htg. with 2 pts. powdered KOH to about 90° see (1) (3); from solid 1,1,2,3,4-pentachlorobutane (3:0750) in 80% yield (2) or from liq. diastereoisomer (3:9068) in 60% yield (2) with Zn dust in alc. see (2).]

$\bar{C}$  on stdg. (1) (2) polymerizes to a dark resinous mass (4).

3:7210 (1) Muskat, Northrup, *J. Am. Chem. Soc.* **52**, 4054-4055 (1930). (2) Prins, *Rec. trav. chim.* **56**, 119-125 (1937). (3) Muskat (to du Pont), U.S. 2,038,693, Apr. 28, 1936; *Cent.* 1936, II 3359; *C.A.* **30**, 3912 (1936). (4) I. G. Farbenindustrie, French 769,472, Aug. 27, 1934; *Cent.* 1935, I 1946.

## 3:7212 CHLOROACETALDEHYDE



B.P. 85-86° (1)  
 85.0-85.5° cor. at 748 mm. (2)  
 84.5-85° at 759 mm. (3)

Colorless liq. with sharp and penetrating odor; vigorously attacks mucous membrane. —  $\bar{C}$  with aq. forms (2) a crystn. hemihydrate,  $\bar{C} \cdot \frac{1}{2}\text{H}_2\text{O}$ ; this does not have a sharp m.p. but about 43-50° begins to liquefy and on further htg. yields  $\bar{C}$ , whose vapor may be dried by passing over anhydr.  $\text{CuSO}_4$  (2) (3); this hemihydrate is sol. in aq. from which it may be recovered by evaporation in a stream of dry  $\text{CO}_2$ ; it is also sol. in alc. or ether, eesp. unchanged on evapn. of solvent (2) (for prepn. (60% yield) from glycerol  $\alpha$ -monochlorohydrin (3:9038) by oxidn. with  $\text{HIO}_4$  see (40)). —  $\bar{C}$  also forms (4) with EtOH a liq. chloroacetaldehyde ethylalcoholate (chloroacetaldehyde ethyl-hemi-acetal), but in excess alc. on protracted stdg. at room temp. (4) this is converted to chloroacetaldehyde diethylacetal (3:8228), or on treatment with dry HCl yields (4)  $\alpha,\beta$ -dichloroethyl ethyl ether (3:5640).

[For prepn. of  $\bar{C}$  from its crystn. trimer (3:2300) by distn. at ord. press. see (2) (5) (6); from chloroacetaldehyde diethylacetal (3:8228) by htg. at 150° in  $\text{CO}_2$  with anhydr. oxalic acid (2), AcOH (2), or dil.  $\text{H}_2\text{SO}_4$  (2) (7) see indic. refs.; from chloroacetaldehyde ethylalcoholate (see above) by htg. with anhydr. oxalic acid at 150° (90% yield) see (8) (note that the netn. of  $\text{Cl}_2$  on paraldhydo (1:0170) gives acc. to conditions either  $\bar{C}$  (9) or  $\alpha,\beta$ -trichloro-*n*-butyraldehyde (butylchloral) (3:5910) (10) (11)].

[For prepn. of  $\bar{C}$  from vinyl chloride (3:7010) with  $\text{Cl}_2$  + aq. in the dark at 35° see (12) (13) (14) (15); from methylene dichloride (3:5020) with formaldehyde +  $\text{SO}_2\text{Cl}_2$  at 300° with cat. see (16); from  $\alpha,\beta$ -dichloroethyl ethyl ether (3:5640) with conc.  $\text{H}_2\text{SO}_4$  see (17); from  $\alpha,\beta$ -dichloroethyl acetate on distn. with a little  $\text{ZnCl}_2$  (acetyl chloride also formed) (18) or from  $\alpha,\beta$ -dichloroethyl benzoate similarly (benzoyl chloride also being formed) (19) or from  $\alpha,\beta$ -dichloroethyl laurate (lauroyl chloride also being formed) (19) see indic. refs.]

[For formn. of  $\bar{C}$  from sodium  $\beta,\beta$ -dichloro- $\alpha$ -hydroxypropionate on boilg. with aq. see (20); from  $\beta$ -chloroethylidene-diurethane on warming with dil. HCl see (21); from acetaldehyde (1:0100) with ethyl hypochlorite followed by distn. with anhydr. oxalic acid see (22); from chloroacetaldehyde-sulfonic acid [Beil. I<sub>2</sub>-(818)] by treatment with steam in 60% H<sub>2</sub>SO<sub>4</sub> (23) or by htg. with 80% H<sub>2</sub>SO<sub>4</sub> (24) see indic. refs.]

$\bar{C}$  gives positive fuchsin-aldehyde test (1). —  $\bar{C}$  reduces NH<sub>4</sub>OH/AgNO<sub>3</sub> on warming (2).

$\bar{C}$  does not oxidize in the air (2) but is oxidized by conc. HNO<sub>3</sub> (2) (20) or by AgOH (20) or by dil. H<sub>2</sub>O<sub>2</sub> (25) to chloroacetic acid (3:1370). —  $\bar{C}$  on treatment as directed (26) with halogen magnesium alcoholate (e.g., EtOMgCl) is reduced to  $\beta$ -chloroethanol (3:5552).

$\bar{C}$  on stdg. in a. t. is rapidly converted to an amorphous polymer (2);  $\bar{C}$  (or its hemihydrate) on shaking with  $\frac{1}{2}$  vol. cold conc. H<sub>2</sub>SO<sub>4</sub> yields (1) a cryst. trimer, 2,4,6-tris-(chloromethyl)-trioxane-1,3,5 (3:2300), m.p. 87–87.5°, which on distn. at ord. press. depolymerizes to  $\bar{C}$ .

The hemihydrate of  $\bar{C}$  htd. alone or in pres. of a few drops of conc. H<sub>2</sub>SO<sub>4</sub> condenses with itself yielding (27) (28)  $\alpha,\gamma$ -dichlorocrotonaldehyde [Beil. I-731, I<sub>2</sub>-(789)].

[ $\bar{C}$  warmed with EtOH (4) or the ethylalcoholate of  $\bar{C}$  in EtOH treated with dry HCl gas (8) yields chloroacetaldehyde diethylacetal (3:8228), b.p. 157°, and in the latter case also (4)  $\alpha,\beta$ -dichloroethyl ethyl ether (3:5640).]

[ $\bar{C}$  with KCN yields (29) (7) an oily prod. (cyanohydrin?) which by hydrolysis with HCl gives  $\beta$ -chlorolactic acid [Beil. III-286, III<sub>1</sub>-(116), III<sub>2</sub>-(209)] + AcOH,  $\bar{C}$  + NaCN + BzCl yields (30)  $\alpha$ -benzoxy- $\beta$ -chlorolactonitrile; note, however, that  $\bar{C}$  boiled with aic. KCN yields (31) EtOAc, or with aq. KCN yields (31) AcOH.]

[For behavior of  $\bar{C}$  with AcCl (2), Ac<sub>2</sub>O (32), see indic. refs.;  $\bar{C}$  with ethyl diazoacetate yields (3) ethyl  $\gamma$ -chloroacetoacetate (3:6375);  $\bar{C}$  with EtMgBr in ether yields (6) 1-chloro-ethyl-2 (3:8025);  $\bar{C}$  with nitromethane as directed (33) yields 1-chloro-3-nitropropanol-2, with nitroethane, 1-chloro-3-nitrobutanol-2;  $\bar{C}$  with thioformamide (35) or  $\bar{C}$  + formamide + P<sub>2</sub>S<sub>5</sub> (34) yields thiazole [Beil. XXVII-15, XXVII<sub>1</sub>-(207)], m.p. 116°.]

— Chloroacetaldoxime: lachrymatory oil dec. on distn. at 10 mm. (36). [From  $\bar{C}$  with 4 moles NH<sub>2</sub>OH.HCl (36).]

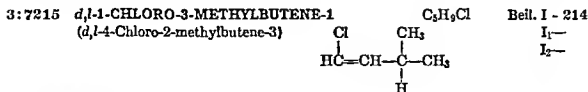
Ⓐ Chloroacetaldehyde semicarbazone: ndls. from alc., m.p. 148° (37), 134–135° dec. (38), 134° (40). [From  $\bar{C}$  + semicarbazide hydrochloride + NaOAc (37).]

— Chloroacetaldehyde dimethone: unreported. [Note that  $\bar{C}$  with warm alc. soln. of "dimethone" ("dimegone") (dimethyldihydroresorcinol) not only condenses normally but also loses HCl yielding (39) same prod., m.p. 227° u c., 237.5° cor. (39), as obtd. from hydroxyacetaldehyde.]

- 3:7212 (1) Jones, Williams, *J. Chem. Soc.* 1934, 834. (2) Natterer, *Monatsh.* 3, 442–464 (1882). (3) Schlotterbeck, *Ber.* 42, 2570–2571 (1909). (4) Natterer, *Monatsh.* 5, 494–499 (1884). (5) Späth, *Monatsh.* 36, 6–7 (1915). (6) Helferich, Speidel, *Ber.* 54, 2634–2635 (1921). (7) Frank, *Ann.* 206, 339–344 (1880). (8) Fritsch, Schumacher, *Ann.* 279, 307–308 (1894). (9) Freundler, *Bull. soc. chim.* (4) 1, 79 (1907). (10) Kramer, Pinner, *Ber.* 3, 385 (1870); *Ann.* 158, 41–42 (1871). (11) Pinner, *Ann.* 179, 26 (1875). (12) Ernst, Lange (to I.C.), U.S. 1,806,285, May 19, 1931; *Cent.* 1931, II 1632; *C. A.* 25, 3671 (1931); *Brit.* 299,319, Oct. 22, 1937; *Cent.* 1930, I 129; *C. A.* 23, 3235 (1929); *Ger.* 496,062, Oct. 23, 1927; *Cent.* 1930, I 3722; *C. A.* 24, 3251 (1930); *French* 662,361, Aug. 6, 1929; *Cent.* 1930, I 129. (13) *Brit.* 299,722, Oct. 28, 1937; *C. A.* 23, 3479 (1929). (14) N. V. de Bataafsche Petroleum Maatschappij, *French* 787,529, Sept. 24, 1935; *Cent.* 1936, II 2227; *C. A.* 30, 1067 (1936). (15) Groll, Hearn (to Shell Development Co.), U.S. 2,060,303, Nov. 10, 1936; *Cent.* 1937, I 4155; *C. A.* 31, 419 (1937). (16) Frohlich, Wierzevich (to Standard Oil Development Co.), U.S. 2,042,303, May 26, 1936; *Cent.* 1936, II 3193; *C. A.* 30, 4871 (1936); *Ger.* 629,897, May 20, 1936; *Cent.* 1936, II 2448; *C. A.* 30, 6006 (1936). (17) Jacobsen, *Ber.* 4, 216 (1871). (18) Soc. des Usines Chimiques Rhone-Poulenc, *Brit.* 329,721, June 19, 1930; *Cent.* 1930, II 1611; *C. A.* 24, 5767 (1930). (19) Soc. des Usines Chimiques Rhone-Poulenc, *Ger.* 527,874, June 22, 1931; *Cent.* 1931, II 1350. (20) Reisse, *Ann.* 257, 234–236 (1890). (21) Houben, *J. prakt. Chem.* (2) 105, 15 (1923). (22) Goldschmidt, Endres, *Dursch. Ber.* 53,

576-577 (1925). {23} Lepouse, *Bull. soc. chim. Belg.* **34**, 141-142 (1925). {24} Chem. Fabrik Weiler-ter-Meer, Ger. 362,744, Oct. 31, 1922; *Cent.* **1923**, II 1246. {25} Filachione, *J. Am. Chem. Soc.* **61**, 1706 (1939). {26} I.G., Brit. 384,156, Dec. 22, 1932; *Cent.* **1933**, I 1351. {27} Natterer, *Monatsh.* **4**, 539-543 (1883). {28} Lespieau, *Bull. soc. chim.* (4) **43**, 200-201 (1928). {29} Glinesky, *Ber.* **6**, 1256-1257 (1873). {30} MacCorquodale, Johnson, *Rec. trav. chim.* **51**, 486 (1932).

{31} Chattaway, Irving, *J. Chem. Soc.* **1929**, 1043. {32} Späth, *Monatsh.* **36**, 36 (1915). {33} I. G. French 804,589, Oct. 27, 1930; *Cent.* **1937**, I 1791; *C.A.* **31**, 3505 (1937). {34} Hromatka (to E. Merck), Ger. 670,131, Jan. 12, 1939; *Cent.* **1939**, I 2296; *C.A.* **33**, 2909 (1939). {35} Willstätter, Wirth, *Ber.* **42**, 1918 (1909). {36} Meister, *Ber.* **40**, 3442 (1907). {37} Blaise, *Bull. soc. chim.* (4) **15**, 671-672 (1914). {38} Kling, *Bull. soc. chim.* (4) **5**, 415 (1909). {39} Vorlander, *Z. anal. Chem.* **77**, 254-255 (1929). {40} Hatch, Alexander, *J. Am. Chem. Soc.* **67**, 688 (1945).

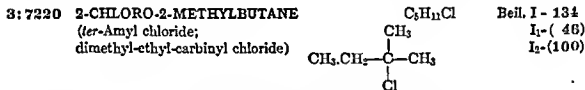


B.P. 85-87° (1)

91-96° (2)

[For prepn. of  $\bar{C}$  from 4,4-dichloro-2-methylbutane (3:7885) with alc. KOH see (1); from 3,4-dichloro-2-methylbutane (3:8075) with alc. NaOH see (2) (note, however, that the latter process very probably leads to a mixt. of  $\bar{C}$  with other prods.).]

**3:7215** (1) Bruylants, *Ber.* **8**, 413-414 (1875). (2) Kondakow, *Ber.* **21** *Referate*, 439 (1888).



B.P.		F.P.	
86°	(1) (2) (11)	-73.7° (9)	$D_4^{20} = 0.8658$ (5)
86.0-86.1°	(3)	-72.7° (4)	0.8650 (28)
85.65°	at 760 mm. (4)	M.P.	
85.4-85.6°	at 762 mm. (5)	-73.3° (9)	$D_4^{13.5} = 0.86989$ (10)
84.5°	at 759 mm. (28)		$n_D^{20} = 1.4058$ (5)
83.0-84.5°	at 744 mm. (6)		1.40520 (28)
51°	at 238 mm. (7)		1.4055 (7)
37-38°	at 150 mm. (8)		$n_D^{13.5} = 1.4082$ (10)

$\bar{C}$  with aq. forms binary const.-boilg. mixt., b.p. 76° (2);  $\bar{C}$  with aq. + *ter*-amyl alc. (1:6160) forms a ternary const.-boilg. mixt. (2).

[For prepn. of  $\bar{C}$  from *ter*-amyl alc. (1:6160) with HCl gas see (11); with conc. HCl (yield: 93-98% (12), 65% (13)) see (12) (13); with  $PCl_3$  (41% yield (6)) or  $PCl_3 + ZnCl_2$  (98% yield (14)) see (6) (14); with  $PCl_5$  (80% yield (14)) see (1) (14); with  $SOCl_2$  (yield: 99% (14), 41% (6)) see (14) (6); with *n*-octyl chloride see (6); with oxalyl chloride (3:5060) (yield 18% (6)) see (15) (6); with diphosgene (3:5515) see (16); with *p*-nitrobenzoyl chloride see (17).]

[For prepn. of  $\bar{C}$  from isopropyl-methyl-carbinol (2-methylbutanol-3) (1:6170) by

rearr. with conc.  $\text{HCl} + \text{ZnCl}_2$  (80% yield (7)), or with  $\text{HCl}$  on long stdg. (97% yield (7)), or with  $\text{PCl}_5$  (76% yield (7)), or with  $\text{SOCl}_2 + \text{pyridine}$  (73% yield (7)) see (7).]

[For prepn. of  $\bar{\text{C}}$  from trimethylethylene (2-methylbutene-2) (1:8220) by addn. of  $\text{HCl}$  see (18) (19) (20); from isopropylethylene (3-methylbutene-1) (1:8200) see (5).]

[For formn. of  $\bar{\text{C}}$  from 2-methylbutane (isopentane) (1:8500) by shaking 2 min. with diisobutylene hydrochloride (3:8113) +  $\text{AlCl}_3$  see (20).]

$\bar{\text{C}}$  very rapidly loses  $\text{HCl}$  by boilg. aq., e.g., 88.6% in 15 min., 94.9% in 30 min., 95.4% in 60 min. (7) Note that hydrolysis with *hot* aq. or aq.  $\text{Na}_2\text{CO}_3$  gives exclusively olefins (20) (6) but that with *cold* aq. or *cold* aq.  $\text{NaOH}$  some *ter*-amyl alc. (1:6160) is also formed (20), although the latter may result from hydration of the olefin. [For further studies of hydrolysis of  $\bar{\text{C}}$  see (2) (6) (20) (21) (22) ]

$\bar{\text{C}}$  on passing over  $\text{BaCl}_2 + \text{soda-lime}$  at  $350-400^\circ\text{C}$  gives (85% yield (5)) a mixture of trimethylethylene (2-methylbutene-2) (1:8220) + *unsym.*-ethyl-methyl-ethylene (2-methylbutene-1) (1:8210).

$\bar{\text{C}}$  with  $\text{Mg}$  in dry ether gives (yield: 73.6% (23), 38% (26))  $\text{RMgCl}$ ; this with  $\text{CO}_2$  gives (60% yield (13)) dimethyl-ethyl-acetic acid (1:1113) q.v. (see also derivatives below).

$\bar{\text{C}}$  with  $\text{Ag}$  3,5-dinitrobenzoate does not (21) yield expected *ter*-amyl 3,5-dinitrobenzoate

① Dimethyl-ethyl-acetanilide: m.p.  $90-91^\circ$  u.c. (25),  $92^\circ$  cor. (26),  $91.4^\circ$  (27). [From  $\text{RMgCl}$  + phenyl isocyanate (25) (26).] [Note that this same product results by rearr., however, from similar treatment of the  $\text{RMgCl}$  epds. from 3-chlor-2-methylbutane (3:7275) q.v.]

② Dimethyl-ethyl-acet-*p*-toluidide: m.p.  $83.0-83.5^\circ$  u.c. (25),  $83.3^\circ$  (27). [From  $\text{RMgCl}$  + *p*-tolyl isocyanate (25) ]

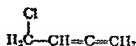
③ Dimethyl-ethyl-acet- $\alpha$ -naphthalide: m.p.  $137-138^\circ$  u.c. (25). [From  $\text{RMgCl}$  +  $\alpha$ -naphthyl isocyanate (25).]

3:7220 (1) Wychnegradsky, *Ann.* 190, 336 (1877). (2) Ayres, *Ind. Eng. Chem.* 21, 899-904 (1929). (3) Brearley, Kistakowsky, Stauffer, *J. Am. Chem. Soc.* 59, 44-46 (1936). (4) Timmermans, *Bull. soc. chim. Belg.* 30, 66 (1921). (5) Leendertse, Tulleners, Waterman, *Rec. trav. chim.* 52, 521-524 (1933). (6) French, Schaefer, *J. Am. Chem. Soc.* 57, 1576-1578 (1935). (7) Whitmore, Johnston, *J. Am. Chem. Soc.* 60, 2265-2266 (1938). (8) Simons, Fleming, Whitmore, Bawinger, *J. Am. Chem. Soc.* 60, 2267-2269 (1938). (9) Turkevich, Smyth, *J. Am. Chem. Soc.* 64, 737 (1942). (10) Jahn, Möller, *Z. physik. Chem.* 13, 389 (1894).

(11) Bruchet, *Ann. chim.* (7) 10, 354 (1897). (12) Norris, Watt, Thomas, *J. Am. Chem. Soc.* 38, 1076 (1916). (13) Corson, Thomas, Waugh, *J. Am. Chem. Soc.* 51, 1950 (1929). (14) Clark, Straight, *Trans. Roy. Soc. Can.* (3) 23, 111 77-89 (1929). (15) Adams, Weeks, *J. Am. Chem. Soc.* 38, 2518-2519 (1916). (16) Nekrasow, Melnikow, *J. prakt. Chem.* (2) 127, 216-217 (1930). (17) Meisenheimer, *Ann.* 442, 202 (1925). (18) Michael, Zeidler, *Ann.* 385, 269-270 (1911). (19) Aschan, *Ber.* 51, 1304-1306 (1918). (20) Woodburn, Whitmore, *J. Am. Chem. Soc.* 56, 1394-1395 (1934).

(21) Hughes, *J. Am. Chem. Soc.* 57, 708-709 (1935). (22) Hughes, McNulty, *J. Chem. Soc.* 1937, 1253-1261. (23) Whitmore, Badertscher, *J. Am. Chem. Soc.* 55, 1562 (1933). (24) Tseng, Chu, *Natl. Central Univ. (Nanking), Sci. Rept., Ser. A-1, No. 2, 5-7* (1931); *C.A.* 26, 2116 (1932); *Cent.* 1939, 1 669. (25) Underwood, Gale, *J. Am. Chem. Soc.* 56, 2119 (1934). (26) Schwartz, Johnson, *J. Am. Chem. Soc.* 53, 1065 (1931). (27) Hommelen, *Bull. soc. chim. Belg.* 42, 240 (1933). (28) Vogel, *J. Chem. Soc.* 1943, 639, 649. (29) Bartlett, Condon, Schneider, *J. Am. Chem. Soc.* 66, 1537 (1944).

### 3:7225 4-CHLOROBUTADIENE-1,2



$\text{C}_4\text{H}_7\text{Cl}$  Beil S.N. 12

B.P.  $88^\circ$  (1)

$\bar{\text{C}}$  represents the initial step in the formn. of 3-chlorobutadiene-1,3 ("Chloroprene") (3:7000) by addn. of aq.  $\text{HCl}$  (1) (2) to vinylacetylene; under certain conditions  $\bar{\text{C}}$  can

be isolated as the major reactn. product, but it readily undergoes isomerization to "Chloroprene" especially in the presence of certain salts, e.g.,  $\text{CuCl}$  (3). When sufficient  $\text{HCl}$  is present the reactn. proceeds further (1) with formn. of 2,4-dichlorobutene-2 (3:5550).

$\bar{\text{C}}$  shaken with 3 pts. 18%  $\text{HCl}$  contg.  $\text{CuCl}$  for 16 hrs. at  $20^\circ$  gives (4) (3) (2) butadiene-1,3 ("Chloroprene") (3:7080), the rest being chloroprene polymer. —  $\bar{\text{C}}$  with 3% dry  $\text{FeCl}_3$  spontaneously evolves heat and yields (4) chloroprene (3:7080).

$\bar{\text{C}}$  stirred with aq.  $\text{Na}_2\text{CO}_3$  at  $60-90^\circ$  for 15 hrs. gives (10) (50% yield (4)) 4-hydroxybutadiene-1,2, colorless lachrymatory, strongly vesicant liq. with sharp pungent odor, misc. aq. and org. solvents, b.p.  $126-128^\circ$  at 756 mm.,  $68-70^\circ$  at 53 mm.,  $D_4^{20} = 0.9164$ ,  $n_D^{20} = 1.4759$ . [This prod. on cat. hydrogenation gives (4) butanol-1 (1:6180) but is unaffected by refluxing with alc.  $\text{NaOEt}$ , 25% aq.  $\text{H}_2\text{SO}_4$ , or 2% aq.  $\text{HCl}$ ; for many other reactns. and derivatives see (4) (10).]

$\bar{\text{C}}$  in 50% alc. or in acetone with  $\text{NaI}$ , stood for 3 hrs. then diluted with aq., gives (46% yield (4)) 4-iodobutadiene-1,2, b.p.  $43-45^\circ$  at 38 mm.,  $D_4^{20} = 1.7129$ ,  $n_D^{20} = 1.5709$  (4), which on btg. at  $125-130^\circ$  polymerizes vigorously to iodoprene. —  $\bar{\text{C}}$  with alc.  $\text{NaCN}$  yields (5) 4-cyanobutadiene-1,3 ( $\beta$ -vinylacrylonitrile), b.p.  $135-138^\circ$  at 760 mm.,  $65-68^\circ$  at 58 mm.,  $48-50^\circ$  at 28 mm.,  $D_4^{20} = 0.8644$ ,  $n_D^{20} = 1.4580$  (5). —  $\bar{\text{C}}$  with liq.  $\text{NH}_3$  at  $-40$  to  $-50^\circ$  yields (6) (7) tris-(butadien-1,2,3-tri-4)amine (for extension to many other amines see (7)).

$\bar{\text{C}}$  added dropwise to 3 vols. conc.  $\text{H}_2\text{SO}_4$  at  $-5^\circ$  to  $+3^\circ$ , then poured onto ice, yields (1) 4-chlorobutanone-2 (3:7640), b.p.  $120-122^\circ$  at 760 mm. (1).

$\bar{\text{C}}$  with  $\text{Cl}_2$  yields (5) (9) mixt. of 2,3,4-trichlorobutene-1 (3:9064) and 1,2,4-trichlorobutene-2 (3:9062) which reacts further to produce 1,2,2,3,4-pentachlorobutane (3:9070).

$\bar{\text{C}}$  in aq.  $\text{Na}_2\text{CO}_3$  suspension, oxidized with  $\text{KMnO}_4$ , yields (1) chloroacetic acid (3:1370), but neither acetic acid nor oxalic acid. —  $\bar{\text{C}}$  in  $\text{CHCl}_3$  treated with  $\text{O}_2$  for 12 hrs. at  $0^\circ$ , then with aq., yields (1) formaldehyde (1:0145) and chloroacetaldehyde (3:7212) (the latter not detected directly but only after  $\text{KMnO}_4$  oxidn. (1) to chloroacetic acid (3:1370)).

3:7225 (1) Carothers, Berchet, Collins, *J. Am. Chem. Soc.* 54, 4066-4070 (1932). (2) Elebanek, Tryurikh, Dolgopolski, *Bull. acad. sci. (U.R.S.S.)* 1933, No. 2, 189-226; *Chem. Rev.* 1933, II 3343 C.A. 30, 1239 (1936) (full English translation in *Rubber Chem. Tech.* 9, 383-408 (1936)). (3) Carothers (to du Pont), U.S. 2,104,789, Jan. 11, 1938; *Chem. Rev.* 1939, I 4108; C.A. 32, 1718 (1938). (4) Carothers, Berchet, *J. Am. Chem. Soc.* 53, 2811-2813 (1933). (5) Coffman, *J. Am. Chem. Soc.* 57, 1981-1984 (1935). (6) I. G. Farbenindustrie, French 515,312, July 9, 1937; *Chem. Rev.* 1937, II 2750; C.A. 32, 958 (1938). (7) Carothers, Berchet (to du Pont), U.S. 2,136,177, Nov. 8, 1938; *Chem. Rev.* 1939, I 2497; C.A. 33, 1344 (1939). (8) Carothers, Berchet, *J. Am. Chem. Soc.* 53, 1628-1631 (1933). (9) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934; *Chem. Rev.* 1933, I 3724; C.A. 28, 5716 (1934). (10) Carothers, Berchet (to du Pont), U.S. 2,073,363, March 9, 1937; *Chem. Rev.* 1933, I 1236; C.A. 31, 3503 (1937).

3:7230 1,1-DICHLOROPROPANE		$\text{CH}_3\text{CH}_2\text{CHCl}_2$	$\text{C}_3\text{H}_4\text{Cl}_2$	Beil. I-105
(Propylidene (di)chloride)				$\text{I}_1$ — $\text{I}_2$ —
B.P. $88.3^\circ$	(1)	$D_4^{20} = 1.1321$ (1)	$n_D^{20} = 1.4288$ (1)	
$87-88^\circ$ at 750 mm.	(2)		1.4295 (2)	
$86.8-87.6^\circ$	(3)			
$86^\circ$	(4)			

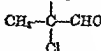
[For prepn. from propionaldehyde (1:0110) with  $\text{PCl}_3$  (36-37% yield (1)) together with other products see (1) (3) (5); for formn. (19.6%) (together with other products) from propane by vapor-phase chlorination at  $400^\circ$  see (6) (7) (8); for formn. from 1-chloropropene-1 (3:7030) by addn. of  $\text{HCl}$  at  $0^\circ$  in presence of  $\text{FeCl}_3$  see (2).]

$\bar{C}$  on hydrolysis yields propionaldehyde (1:0110); for study of behavior of  $\bar{C}$  with boilg. aq. + trace of  $\text{NaHCO}_3$  or with boilg. aq. + Fe see (6).

$\bar{C}$  with alc. KOH yields (5) 1-chloropropene-1 (3:7030) q.v.

3:7232 (1) *Ann. Chem. Soc.* 63, 2477 (1941). (2) Kharasch, Engel-  
 1935).  
 11 458-  
 1941).  
 Hass,  
 June 4, 1935; *Cent.* 1936, 1 1500.

3:7235  $\alpha$ -CHLORO-ISOBUTYRALDEHYDE  $\text{CH}_3$   $\text{C}_4\text{H}_7\text{OCl}$  Beil. I - 676  
 (2-Chloro-2-methylpropanal-1)



I<sub>1</sub>—  
 I<sub>2</sub>—

B.P. 90° (1) (2)

$D_4^{15} = 1.053$  (1) (2)

Colorless liq with piquant odor suggestive of chloral.

[For prepn. of  $\bar{C}$  from 2-methylpropanol-1 (isobutyl alc.) (1:6165) with  $\text{Cl}_2$  see (1) (2); from  $\alpha,\beta$ -dichloroisobutyl isobutyl ether (see below) by hfg. with aq. at 100° see (1) (2); from  $\alpha$ -chloroisobutyraldehyde diisobutylacetal (see below) with anhydrous oxalic acid (1:0535) or with  $\text{Ac}_2\text{O}$  (1:1015) on hfg. see (2);  $\bar{C}$  is not (2) formed by chlorination of isobutyraldehyde (1:0120).]

$\bar{C}$  reduces Tollens' reagent, Fehling's soln., or  $\text{KMnO}_4$  (1) (2);  $\bar{C}$  on oxidn. with alk.  $\text{KMnO}_4$  yields (2)  $\alpha$ -hydroxyisobutyric acid (1:0431), m.p. 79°.

$\bar{C}$  adds  $\text{NaHSO}_3$  yielding a compd. from which  $\bar{C}$  is regenerated with difficulty (1) (2).

$\bar{C}$  on shaking with conc.  $\text{H}_2\text{SO}_4$  (3/5 vol.) yields (1) (2) the corresp. trimer, viz., para- $\alpha$  chloro-isobutyraldehyde (2,4,6-tris-( $\alpha$ -chloroisopropyl)trioxane-1,3,5) (3:3220), m.p. 107° (1) (2).

[ $\bar{C}$  with isobutyl alc. (1:6165) treated with  $\text{HCl}$  gas gives (2)  $\alpha,\beta$ -dichloroisobutyl isobutyl ether, b.p. 192.5° at 760 mm., 83° at 15 mm.,  $D_4^{15} = 1.031$ ,  $n_D^{19} = 1.437$  (2), also obtd. from isobutyl alc. directly with  $\text{Cl}_2$  in the cold (2); note that this prod. with aq. on hfg. gives  $\bar{C}$  +  $\alpha$ -chloroisobutyraldehyde di-isobutylacetal, h.p. 218° at 760 mm., 102° at 15 mm.,  $D_4^{15} = 0.9355$ ,  $n_D^{17} = 1.428$  (2).]

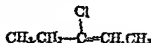
[ $\bar{C}$  (or the above  $\alpha$ -chloroisobutyraldehyde di-isobutylacetal) with ethyl carbamate acid. with  $\text{HCl}$  gas gives (2)  $\alpha$ -chloroisobutyridene bis-urethane  $(\text{CH}_3)_2\text{C}(\text{Cl})\cdot\text{CH}(\text{NH}\cdot\text{COOC}_2\text{H}_5)_2$ , m.p. 122° (2).]

[For complex behavior of  $\bar{C}$  with  $\text{MeMgBr}$  see (3).]

—  $\alpha$ -Chloro-isobutyraldoxime: m.p. 96-97° (4). [Prepd. indirectly from isobutylene with amyl nitrite +  $\text{HCl}$  (4).]

3:7235 (1) Brochet, *Bull. soc. chim.* (3) 7, 641-644 (1892). (2) Brochet, *Ann. chim.* (7) 10, 352-362 (1897). (3) Henry, *Bull. acad. roy. Belg.* 1907, 163-189; *Cent.* 1907, II 445; *Rec. trav. chim.* 26, 410, 425-429 (1907); *Compt. rend.* 144, 308 (1907). (4) Ipatiev, Ssoulonina, *J. Russ. Phys.-Chem. Soc.* 33, 496-501 (1901); *Cent.* 1901, II 1201.

3:7240 3-CHLOROPENTENE-2



$\text{C}_5\text{H}_9\text{Cl}$

Beil. I —

I<sub>1</sub>—  
 I<sub>2</sub>-(185)

B.P. 01-02° (1)

$D_{20}^{20} = 0.9125$  (2)

$n_D^{20} = 1.423$  (1)

00-02° at 781 mm. (2)



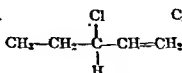
Two geometrical stereoisomers of  $\bar{C}$  are possible but as yet unrecognized.

[For prepn. of  $\bar{C}$  (together with 2-chloropentene-2 (3:7285) and other prods.) from methyl *n*-propyl ketone (1:5415) with  $PCl_5$  see (1); for prepn. of  $\bar{C}$  (together with other prods.) from diethyl ketone (propione) (1:5420) with  $PCl_5$  (1) followed by treatment with alc. KOH (2) see (1) (2).]

$\bar{C}$  with  $NaNH_2$  in xylene at  $130^\circ$  gives (3) a little pentyne-2 (1:8040) and on subsequent pouring of the reactn. mixt. into water also pentyne-1 (1:8025).

3:7240 (1) D. ... 3:7240 (1) D. ... 3:7240 (1) D. ... 3:7240 (1) D. ... 3:7240 (1) D. ... (3)

3:7260 3-CHLOROPENTENE-1  
( $\alpha$ -Ethylallyl chloride)



$\text{C}_5\text{H}_9\text{Cl}$

Beil. I—

I—

I—(182)

B.P.  $93-94^\circ$  at 759.3 mm. (1)

$92-93^\circ$  (2) (3)

$50-50.2^\circ$  at 150 mm. (5)

$D_4^{20} = 0.8978$  (1) .  $n_D^{20} = 1.4254$  (1)

$n_D^{25} = 1.4234$  (4)

Note:  $\bar{C}$  by virtue of facile allylic transposition is readily converted to an equilibrium mixt. with its synionic isomer, 1-chloropentene-2 (3:7470) q.v.; reactns. of  $\bar{C}$  may therefore frequently yield also the corresponding derivatives of the isomer.

[For prepn. of  $\bar{C}$  (or its mixt. with 1-chloropentene-2 (3:7470)) from ethyl-vinyl-carbinol (penten-1-ol-3) with dry  $\text{HCl}$  (1) (3) (5) (7), with aq.  $\text{HCl}$  at  $0^\circ$  (6), with  $PCl_5$  at  $45^\circ$  (4) or in cold with pyridine (7) or dimethylaniline (7) (55-59% (7)), with  $\text{SOCl}_2$  alone (24% yield (7)) or in ether (24% yield (7)), or with dimethylaniline (43% yield (7)) see indic. refs.] [ $\bar{C}$  is separable from the accompanying isomer by careful fractional distillation (5) (7).]

$\bar{C}$  on long shaking with aq.  $\text{Na}_2\text{CO}_3$  gives (7) in very poor yield penten-1-ol-3 accompanied by much penten-3-ol-1 and other products. —  $\bar{C}$  with alc.  $\text{NaOEt}$  gives (4) the corresp. ethyl ether, viz., 3-ethoxypentene-1, b.p.  $102^\circ$ ,  $D_4^{25} = 0.7768$ ,  $n_D^{25} = 1.3986$ , accompanied by the isomeric 1-ethoxypentene-2, b.p.  $123^\circ$ ,  $D_4^{25} = 0.7930$ ,  $n_D^{25} = 1.4099$  (4).

[For extensive study of behavior of  $\bar{C}$  with  $\text{KOAc} + \text{AcOH}$ , with  $\text{AgOAc}$ , with *N*-methylaniline, with diethylamine, etc., see (7); for reactn. of  $\bar{C}$  with phenol in pres. of  $\text{K}_2\text{CO}_3 + \text{acetone}$  see (5).]

① *N*-(Penten-1-yl-3)phthalimide (*N*-( $\alpha$ -ethylallyl)phthalimide): colorless cryst. from alc., m.p.  $78-79^\circ$  (7). [From  $\bar{C}$  on bkg. with  $\text{K}$  phthalimide in a s.t. at  $190-200^\circ$  for  $2\frac{1}{4}$  hrs.; yield is only about half that obt'd. from 1-chloropentene-3, the corresp. deriv. of which always accompanies that from  $\bar{C}$  (7).]

3:7260 (1) Baudrenghien, *Bull. soc. chim. Belg.* 37, 338 (1923). (2) Mumm, Richter, *Ber.* 73, 858-860 (1940). (3) Mumm, Hornhardt, Diederichsen, *Ber.* 72, 107 (1939). (4) Prevost, *Compt. rend.* 187, 1053-1054 (1928). (5) Lauer, Filbert, *J. Am. Chem. Soc.* 58, 1388 (1936). (6) Prevost, *Bull. soc. chim.* (4) 49, 264-267 (1931). (7) Meisenheimer, Link, *Ann.* 479, 254-277 (1930).

3: 7265 $\beta$ -CHLOROETHYL METHYL ETHER		$C_3H_7OCl$	Beil. I - 337
( $\beta$ -Methoxyethyl chloride)		$CH_2O.CH_3$	I <sub>1</sub> -(170)
		$ $	I <sub>2</sub> -(335)
		$CH_2Cl$	
B.P.			
02-93°	(1) (2)	$D_4^{20} = 1.0345$ (1)	$n_D^{20} = 1.41112$ (4)
01°	(5)	1.0460 (4)	1.411 (1)
90-91°	at 735.7 mm. (3)		
90.5°	at 747 mm. (7)	$D_4^{15} = 1.0407$ (4) (1)	
89.4-80.7°	at 763.8 mm. (4)		

Colorless liq. with odor like  $CHCl_3$ ; does not fume in air (3). — Sol. in aq. at room temp. to extent of 8% by wt. (7).

[For prepn. from ethylene chlorohydrin (3:5552) +  $(CH_3)_2SO_4$  (60% yield (2)) see (2); for prepn. from  $\beta$ -methoxyethanol (1:6405) with  $PCl_3$  + pyridine (65% yield (6)), or  $SOCl_2$  + dimethylamine (7), or diazomethane (5) see (6) (5) (7); for prepn. from ethylene +  $N,N$ -dichlorobenzene sulfonamide see (1).]

$\bar{C}$  on shaking with aq. does not hydrolyze (dif. from  $\alpha$ -chloroethers).

3: 7265 (1) Sklyarov, *J. Gen. Chem. (U.S.S.R.)* 9, 2121-2125 (1939); *C.A.* 34, 4055 (1940). (2) Jones, Powers, *J. Am. Chem. Soc.* 46, 2531-2532 (1924). (3) Fietti, de Gaspari, *Gazz. chim. ital.* 27, II 293 (1897). (4) Karvonen, *Ann. Acad. Sci. Fennicae* 3-A, No. 7, 1-103 (1912); *Cent.* 1912, II 1269; *C.A.* 14, 2175 (1920). (5) Meerwein, Hinz, *Ann.* 484, 17 (1930). (6) Palomaa, Kenetli, *Ber.* 64, 798 (1931). (7) Bennett, Heathcoat, *J. Chem. Soc.* 1929, 270.

3: 7270 ISOBUTYRYL CHLORIDE		$CH_3CH-C=O$	$C_4H_7OCl$	Beil. II - 203
		$ $		II <sub>1</sub> -(128)
		$CH_3$		II <sub>2</sub> -(262)
		$ $		
		$Cl$		
B.P.				F.P.
02°	(1) (2)	$-00°$ (7)	$D_4^{20} = 1.0174$ (8)	$n_D^{20} = 1.40789$ (8)
91.5-92.5°	at 748.2 mm. (8)			1.4080 (3)
91-92°	(3)			1.4070 (5)
90-92°	(30)			
91°	at 735 mm. (4)			
90-91°	(5)			
85-88°	at 680 mm. (6)			

[For prepn. of  $\bar{C}$  from isobutyric acid (1:1030) with  $PCl_3$  (81% yield (9)), with  $PCl_3$  (yield: 94% (6), 75% (2)) (8) (4), with  $PCl_3$  +  $ZnCl_2$  (92% yield (9)), with  $SOCl_2$  (yield: 90% (30), 75% (4) (5), 70% (10), 44% (9)), with benzoyl chloride (82-88% yield (13)), or with  $SiCl_4$  in xylene (52% yield (11)) see indic. refs.; for prepn. of  $\bar{C}$  from sodium isobutyrate with  $POCl_3$  see (1) (12).]

[ $\bar{C}$  with isobutyric acid (1:1030) (14) or  $\bar{C}$  with pyridine in ether (15) yields isobutyric anhydride (1:1110), b.p. 182.5°.]

[ $\bar{C}$  on passing over Ni at 420° dec. (15) into  $HCl$ ,  $CO$ ,  $CO_2$ ,  $H_2$ ,  $CH_4$  + propylene;  $\bar{C}$  +  $NH_3$  over  $Al_2O_3$  at 490-500° yields (17) isobutyronitrile, b.p. 108°.]

[ $\bar{C}$  with  $Et_3N$  in dry ether or lgr. at room temp. gives (18) 95% yield triethylamine hydrochloride + 57% yield dimethylketene dimer, cf. also (19) (20).]

[ $\bar{C}$  with  $Cl_2$  (31) in  $CCl_4$  gives (12) cf. (21) 60-70%  $\alpha$ -chloroisobutyryl chloride (3:5385) + 30-40%  $\beta$ -chloroisobutyryl chloride (3:9101);  $\bar{C}$  with  $SO_2Cl_2$  in pres. of dibenzoyl peroxide gives (22) 20%  $\alpha$ -chloroisobutyryl chloride (3:5385) + 80%  $\beta$ -chloroisobutyryl



see indicated refs.] [Note that  $\bar{C}$  cannot be prepd. from the corresp. alc., 2-methylbutanol-3 (1:6170) + HCl since only *ter*-amyl chloride (3:7220) results (11).]

[For formn. of  $\bar{C}$  from either 2-methylbutene-1 (1:8210) or 2-methylbutene-2 (1:8220) at  $-80^\circ$  in presence of  $AlCl_3$  see (7); from isoamyl alcohol (1:6200) + HCl over  $Al_2O_3$  at  $430^\circ$  see (8); from isoamyl chloride (3:7365) over  $ThCl_4$  or  $BaCl_2$  at  $250^\circ$ , finally over pumice at  $200^\circ$ , see (9); from 2-methylbutane (1:8500) +  $Cl_2$  see (10) (1).]

[For study of reactn. of  $\bar{C}$  with Na see (12) (13).]

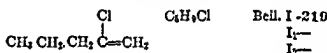
$\bar{C}$  with Mg in dry ether yields (1) (2) corresponding R.Mg.Cl whose treatment with dry  $O_2$  followed by hydrolysis yields (1) (2) 2-methylbutanol-3 (1:6170); [3,5-dinitrobenzoate, cryst. from dil. MeOH (1) or dil. EtOH (2), m.p.  $76^\circ$  (1) (2); *N*-( $\alpha$ -naphthyl)-carbamate, cryst. from pct. eth., m.p.  $111-112^\circ$  (2) (1).] — This R.Mg.Cl should also react according to method of (11) with phenyl isocyanate to yield isopropyl-methyl-acetanilide, m.p.  $78.4^\circ$  (14),  $75^\circ$  (15), although the execution of this reactn. is not recorded.

$\bar{C}$  with excess  $N/10$   $AgNO_3$  is practically completely hydrolyzed in 60 hrs. (2) [dif. from isoamyl chloride (3:7365) which reacts only to extent of 3-4%].

3:7275 (1) Hass, McBee, Weber, *Ind. Eng. Chem.* 27, 1192-1195 (1935). (2) Whitmore, Johnston, *J. Am. Chem. Soc.* 55, 5020-5022 (1933). (3) Wyschnegradsky, *Ann.* 100, 357 (1877). (4) Leendertse, Tulleners, Waterman, *Rec. trav. chim.* 52, 519 (1933). (5) Berthelot, *Ann.* 127, 71 (1863). (6) Wurtz, *Ann.* 129, 368 (1864). (7) Leendertse, Tulleners, Waterman, *Rec. trav. chim.* 53, 717 (1934). (8) Sabatier, Mailhe, *Compt. rend.* 169, 124 (1919). (9) Sabatier, Mailhe, *Compt. rend.* 150, 658 (1913). (10) Aschan, *Cent.* 1918, 11 939.

(11) Underwood, Gale, *J. Am. Chem. Soc.* 56, 2117 (1934). (12) Morton, LeFevre, Hechenbleikner, *J. Am. Chem. Soc.* 58, 757 (1936). (13) Morton, Hechenbleikner, *J. Am. Chem. Soc.* 58, 1699 (1936). (14) Himmelen, *Bull. soc. chim. Belg.* 42, 249 (1933). (15) Crossley, Perkin, *J. Chem. Soc.* 73, 17 (1898).

### 3:7280 2-CHLOROPENTENE-1



B.P.  $95-97^\circ$  (1)

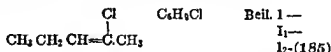
The structure of this material is inadequately supported; the prod. may very possibly be identical with 2-chloropentene-2 (3:7285) q.v.

[For prepn. of  $\bar{C}$  from 2,2-dichloropentane (3:7755) with alc. KOH see (1).]

$\bar{C}$  on further treatment with alc. KOH yields (1) pentyne-1 (1:8025), b.p.  $39.7^\circ$ .

3:7280 (1) Bruylants, *Ber.* 8, 411 (1875).

### 3:7285 2-CHLOROPENTENE-2



B.P.  $95-97^\circ$  (1)

$D_4^{24} = 0.903$  (2)

$n_D^{24} = 1.421$  (2)

$88-89^\circ$  at 760 mm. (2)

$45^\circ$  at 130 mm. (2)

Two geom. stereoisomers of  $\bar{C}$  are possible but as yet unrecognized.

[For prepn. of  $\bar{C}$  from 2,2-dichloropentane (3:7755) with boilg. 10% alc. KOH see (1); from pentanone-2 (1:5415) with  $PCl_5$  see (2).]

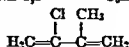
$\bar{C}$  with conc.  $H_2SO_4$  followed by aq. yields (1) methyl-*n*-propyl ketone (pentanone-2 (1:5415), b.p.  $102^\circ$ ).

[ $\bar{C}$  with  $NaNH_2$  in xylene at  $130^\circ$  followed by ice water gives (3) pentyne-1 (1:8025).]

$\bar{C}$  on oxidn. with  $KMnO_4$  yields (1) propionic acid (1:1025) + AcOH (1:1010).

3: 7285 (1) Lemke, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 7, 1995-1998 (1937); *Cent.* 1939, I 2398; *C.A.* 32, 482 (1938). (2) Bourgeul, *Ann. chim.* (10) 3, 369-370 (1925); *Bull. soc. chim.* (4) 35, 1633 (1924). (3) Bourgeul, *Ann. chim.* (10) 3, 220, 370 (1925).

3: 7290 3-CHLORO-2-METHYLBUTADIENE-1,3  $C_5H_7Cl$  Beil S.N. 12  
(2-Chloro-3-methylbutadiene-1,3;  
"β-Chloroisoprene")



B.P. 93° at 760 mm. (1)

$D_4^{20} = 0.9593$  (1)

$n_D^{20} = 1.4689$  (1)

41° at 113 mm. (1) (2)

37° at 105 mm. (1)

[For prepn. of  $\bar{C}$  (40% yield (1)) from 2-methylbutene-1-yne-3 by treatment as specified (1) with  $HCl + Cu_2Cl_2 + NH_4Cl$  see (1) (2) (10); for prepn. (60% yield (3) (4)) from 2,3,3-trichloro-2-methylbutane (3:4755) with quinoline (2 moles) at 140-225° see (3) (4).]

$\bar{C}$  readily polymerizes; for details see (1) (2). [For prepn. of plastic polymers from  $\bar{C}$  see (5).]

$\bar{C}$  htd. in s.t. 16 hrs. at 160° with  $SO_2$  in ord. (not dry) ether yields (6) (7) (10) by 1,4-addition a compd. designated (6) (7) as 1,1-dioxo-3-chloro-4-methylthiascyclopentene-3, ndls. from aq. (7) or alc. (6), m.p. 120.0-120.5° (6) (7). [For extensive study of this prod. see (7).] [The corresponding selenium analog, in very poor (2%) yield from  $\bar{C} + SeO_2$  in  $CHCl_3$  (8), has m.p. 110° dec. (8).]

$\bar{C}$  (1 g.) with 1,4-naphthoquinone (1:9040) htd. at 100° for  $\frac{1}{2}$  hr. gives (1) on cooling 2-chloro-3-methyltetrahydroanthraquinone, white ndls. from acetone, m.p. 165-166° u.c. (1); this prod. on suspension in dil. alc. NaOH and oxidn. of the blue soln. with air until yel., followed by dilution with aq., gives (1) 2-chloro-3-methylanthraquinone, cryst. from AcOH, m.p. 214-215° u.c. (1), 215° u.c. (9).

3: 7290 (1) Carothers, Coffman, *J. Am. Chem. Soc.* 54, 4074-4076 (1932). (2) Carothers, Coffman (to du Pont), U.S. 1,950,441, March 13, 1934; Ger. 588,708, Nov. 24, 1933; Brit. 395,301, Oct. 10, 1933; *Cent.* 1934, II 1038. (3) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 6, 1116-1132 (1936); *Cent.* 1937, I 573; *C.A.* 31, 1003 (1937). (4) Tishchenko, *Russ.* 44,249, Sept. 20, 1935; *Cent.* 1936, I 3575; *C.A.* 32, 2962 (1938). (5) du Pont Co., Brit. 529,838, Nov. 29, 1940; *C.A.* 35, 7758 (1941); French 853,478, Mar. 20, 1940; *C.A.* 35, 2650 (1942). (6) Backer, Strating, *Rec. trav. chim.* 53, 542-543 (1934). (7) Backer, van der Baan, *Rec. trav. chim.* 56, 181-185 (1937). (8) Backer, Strating, *Rec. trav. chim.* 53, 1118 (1934). (9) Keimatsu, Hirano, *J. Pharm. Soc. Japan* 49, 140-147 (1929); *C.A.* 23, 3466 (129). (10) Backer, Blass, *Rec. trav. chim.* 61, 785-801, 924 (1942); *Cent.* 1943, I 1567-1569; *C.A.* 38, 3646-3647 (1944).

3: 7295 ETHYL CHLOROFORMATE  $ClCO.OC_2H_5$   $C_4H_5O_2Cl$  Beil III-10  
("Ethyl chlorocarbonate") III-(5)  
III-(10)

B.P.

F.P.

95° at 760 mm. (1)

-80.6° (1)  $D_4^{25} = 1.127$  (10)

94-95° cor. (2)

$n_D^{15} = 1.3949$  (5)

94° at 773 mm. (3)

$D_4^{20} = 1.13519$  (4)

93.1° at 760 mm. (4)

1.1377 (6)

93.0° at 760 mm. (5)

$n_D^{20} = 1.39738$  (4)

92.6-93.0° at 768 mm. (6)

92.5-93.5° (7)

$D_4^{15} = 1.14419$  (4)

91.3-91.35° at 729.6 mm. (8)

1.1418 (9)

91.5° (10)

See Note 1.

Note 1. For  $D_4^t$  between -75.5° (1.278) and -84.8° (1.022) see (10).